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# ANTHRACEN



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# ANTHRACEN

ITS

CONSTITUTION, PROPERTIES, MANUFACTURE, AND DERIVATIVES

INCLUDING

ARTIFICIAL ALIZARIN, ANTHRAPURPURIN, &c.

WITH THEIR APPLICATIONS IN

DYEING AND PRINTING

BY G. AUERBACH.

TRANSLATED AND EDITED FROM THE REVISED MANUSCRIPT OF THE AUTHOR

BY

WILLIAM CROOKES, F.R.S. &c.

VICE-PRESIDENT OF THE CHEMICAL SOCIETY

EDITOR OF 'THE CHEMICAL NEWS' AND 'QUARTERLY JOURNAL OF SCIENCE'  
AUTHOR OF 'A HANDBOOK OF DYING AND CALICO-PRINTING' 'SELECT METHODS OF CHEMICAL  
ANALYSIS' 'THE MANUFACTURE OF BEET ROOT SUGAR IN ENGLAND' ETC.

LONDON

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1877

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## EDITOR'S PREFACE.

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MR. G. AUERBACH's monograph on Anthracen and its Derivatives is generally recognised both by manufacturers and by scientific theorists as the authority on this interesting and important section of organic chemistry. It presents us with a summary of all important researches on the subject, compiled and digested by one who has made the anthracen derivatives his speciality, and who has had great practical experience in some of the most eminent establishments for the manufacture of artificial alizarin. An English version of this work has been for some time considered as a desideratum by all persons interested in the production and in the application of artificial colouring matters.

The present edition is founded upon a manuscript copy carefully revised and extended by the author so as to embrace all the most recent improvements.

All temperatures throughout the work are stated according to the Centigrade scale, and the specific gravities of liquids are given as on Baumé's hydrometer.



## AUTHOR'S PREFACE.

---

WHEN the first German edition of this book (Seehagen, Berlin) appeared four years ago, it was my purpose to render it as complete as possible, so that every one might find in this monograph all researches bearing upon Anthracen and its Derivatives duly classified, without requiring to search for the memoirs scattered through scientific journals. But if this object was almost attained four years ago, so many novel and important facts have been ascertained since that date, that the book requires to be remodelled and rendered complete. Thus, in a technological point of view, we may instance the discovery of accurate methods for determining the value of anthracen, whereby the utterly untrustworthy processes with alcohol and bisulphide of carbon have been superseded; further, the researches on the formation of alizarin from monosulphanthraquinonate of soda, &c. On the other hand, in the purely scientific region we may mention the beautiful researches of Baeyer and Caro on the synthesis of anthraquinon derivatives from phthalic acid and phenolen; the investigations of Lieber-

mann on chrysammic acid, and many other investigations of distinguished interest.

In general, the plan of the earlier edition has been adhered to, but has been rendered more systematic. The isomeric compounds have been arranged in groups so as to admit of an easier survey. The arrangement of the bibliographical appendix has been retained as far as practicable.

In order that the work may fulfil its object as a complete monograph of Anthracen and its Derivatives, I respectfully request all chemists engaged in the study of this subject to point out to me any memoirs which may have escaped my notice, and kindly to forward me copies of the journals in which such researches have appeared.

May the work serve to draw increased attention to the study of this interesting compound and of its derivatives!

G. AUERBACH.

SADBURY, MIDDLESEX :

*September 1876.*

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## ANTHRACEN AND ITS DERIVATIVES.

---

IN the year 1832 Dumas and Laurent discovered a hydrocarbon, which they obtained from those portions of coal-tar which boil at the highest temperature. From their analyses they deduced the formula  $C_{16}H_{12}$ , and as this formula was  $1\frac{1}{2}$  times the molecular weight of naphthalin, they named the newly discovered body paranaphthalin. Laurent, who examined this compound further, and described some of its derivatives, proposed the name of Anthracen in place of paranaphthalin. He was led to this change by the consideration that a number of hydrocarbons, polymeres of naphthalin, were present in coal-tar, all of which were entitled to the generic appellation of paranaphthalin. The name anthracen appeared to him also better fitted for forming the names of the derivatives according to his system, e.g. anthracenuse. The next addition to our knowledge of this body was due to Fritzsche in 1857. He described a solid hydrocarbon, obtained from coal-tar, to which he attributed the formula  $C_{14}H_{10}$ , and pointed out that this compound had many properties in common with Laurent's anthracen, but differed from it essentially in many others. Thus Dumas and Laurent had observed the melting-point at  $180^{\circ}$ , whilst Fritzsche found it  $210^{\circ}$ . The latter chemist, on its analysis, obtained numbers exactly corresponding with the formula  $C_{14}H_{10}$ , which was confirmed by the composition of the picrate  $C_{14}H_{10}C_6H_2(NO_2)_3OH$ . Fritzsche, therefore, left the identity of the

compound which he had examined, with Laurent's anthracen, an open question, and gave no name to the compound. Shortly afterwards Anderson made an extended investigation of the solid constituents of tars boiling at high temperatures, and published his results in 1862. He described under the name of anthracen a hydrocarbon of the same formula as that discovered by Fritzsche, and prepared from it a series of interesting derivatives. Although many of his observations differed essentially from Laurent's statements, he retained the name given by the latter chemist. He also declared his anthracen identical with the hydrocarbon of Fritzsche. In 1866 Limpricht discovered the synthetic formation of this body by heating the chloride of benzyl to  $180^{\circ}$  with water. In the same year Berthelot announced that anthracen is formed from various more simple hydrocarbons by the action of heat. He found that toluol alone, or a mixture either of styrol and benzol or of benzol and ethylen, yielded anthracen if passed through an ignited tube. At the same time he made a communication on the extraction of anthracen from tar, confirmatory of the views of Anderson. A year later (1867) Fritzsche returned to the hydrocarbon which he had previously described, giving an account of its purification and of its physical properties, and of one of its derivatives, of importance as a reagent. In opposition to Anderson and Berthelot, he contested its identity with anthracen. In 1868 Graebe and Liebermann discovered that a hydrocarbon could be obtained from alizarin by reduction, possessing the same properties as Anderson's anthracen.

Whilst Berthelot, Limpricht, Graebe, and Liebermann regarded the hydrocarbon described by Anderson as a chemical individual, Fritzsche considered it as a mixture of two bodies, which he named photen and phosen. Anderson's anthracen and Fritzsche's photen, however, scarcely differ from each other in their properties. The melting-point is the same, and the accounts as to solubility and behaviour

with reagents show no discrepancy. The diversity existing as to the magnitude of the crystals and as to fluorescence only proves that Fritzsche succeeded in preparing anthracen absolutely free from the foreign admixtures which still adhere to Anderson's specimens. But that anthracen is a distinct chemical entity may be inferred with certainty from the derivatives obtained both by Anderson and by Graebe and Liebermann, all of which appear as well-characterised chemical compounds. It is, however, by no means denied that other hydrocarbons with high boiling-points may be found in coal-tar. Berthelot, indeed, has shown the existence of compounds, which he has named acenaphten and fluoren, and his statement is confirmed by Graebe and Liebermann.

Dumas and Laurent have doubtless examined an anthracen mixed with these compounds. That the substance described by these chemists is to be regarded thus, and not with Berthelot as methylantracen, appears from the following reasons. Dumas and Laurent obtained their paranaphthalin from that portion of coal-tar which boils at high temperatures, just as Anderson procured the hydrocarbon which he describes. Their description agrees perfectly with an impure anthracen. Their published analyses show too little hydrogen for methylantracen. The carbon is too low both for methylantracen and for anthracen, and is therefore untrustworthy, the sum of the percentage of carbon and hydrogen being notably below 100.

|                   |   |   |             | calculated for |                |
|-------------------|---|---|-------------|----------------|----------------|
|                   |   |   |             | $C_{15}H_{12}$ | $C_{14}H_{10}$ |
| Dumas and Laurent |   |   |             |                |                |
| C.                | . | . | 92.22       | 93.75          | 94.38          |
| H.                | . | . | 6.05        | 6.25           | 5.62           |
|                   |   |   | <hr/> 98.27 | <hr/> 100.00   | <hr/> 100.00   |

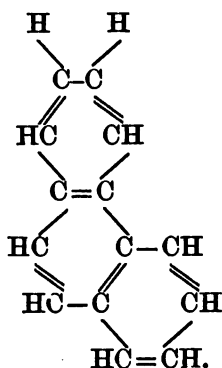
The vapour density as determined by Dumas, 6.74 (Troost, 6.3,  $C_{14}H_{10}$  requiring 6.17, and  $C_{15}H_{12}$  6.65), can



afford no proof, since the specimen employed, according to its description, did not possess the character of purity. Laurent's anthracenuse, however, proves more decidedly the correctness of the view of Graebe and Liebermann. This compound is identical with Anderson's oxanthracen, the anthrachinon (anthraquinon) of Graebe and Liebermann, as was already assumed by Kraut in Gmelin's 'Handbuch.' The earlier analyses of Laurent agree distinctly with the formula  $C_{14}H_8O_2$ , but very badly with his own  $C_{15}H_8O_2$ . The properties of this oxidation-product, so highly characteristic of anthracen, leave no doubt that Laurent obtained anthraquinon in a state of purity, and that the substance from which it was prepared must have consisted mainly of anthracen.

*Constitution of Anthracen and its Derivatives.*

Graebe and Liebermann were the first to express the view that anthracen was formed of three benzol rings, in the same manner as naphthalin of two. The following formula shows how the chemical structure of anthracen is to be regarded upon this hypothesis :



The reasons which Graebe and Liebermann adduce for this view depend, firstly, upon Kekule's theory of the aromatic compounds, and secondly, upon the assumption that naphthalin is formed of two benzol-nuclei.

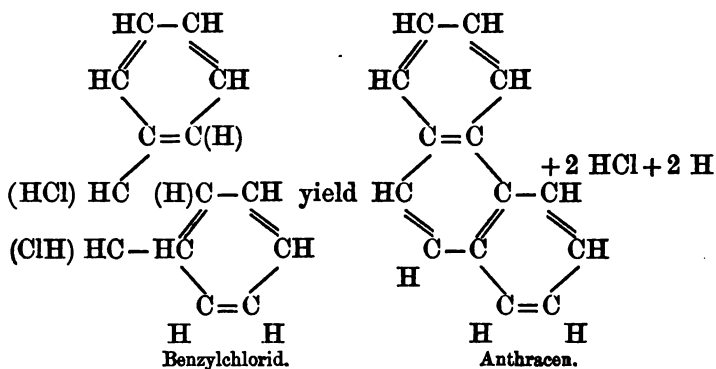
According to the synthesis discovered by Limpricht, two principal products are obtained on heating chloride of benzyl,  $C_6H_5(CH_2Cl)$ , with water in sealed tubes to  $180^\circ$ ,—anthracen and dibenzyl. Two molecules of benzylchloride attach themselves to each other, losing two molecules of hydrochloric acid and two atoms of hydrogen. The latter act upon two other molecules of benzylchloride, and occasion the formation of dibenzyl, which may here be left out of consideration. The formation of anthracen corresponds to the following equation :



The simplest inference from this reaction would be the assumption that anthracen might be regarded as diphenylacetylen ( $C_6H_5C \equiv C(C_6H_5)$ ), the chlorine and hydrogen atoms of the lateral catenæ being eliminated during its formation from benzylchloride. But even before the publication of the most recent researches of Limpricht and Schwapert, Graebe and Liebermann pronounced this view inaccurate, in consequence of the derivation of alizarin from anthracen. As the tinctorial body just named yields on oxidation phthalic acid, it cannot be regarded as a derivative of diphenylacetylen, since these derivatives must yield on oxidation, benzoic acid or substituted benzoic acids. In the meantime, Limpricht and Schwanert obtained tolen, which from its formation and properties must indubitably be regarded as diphenylacetylen, which proves the correctness of the assumption, that the constitution of anthracen must be different. Graebe and Liebermann were led by the similarity of anthracen and naphthalin to their view as to the collocation of the atoms in anthracen, as figured above, with which the formation of this hydrocarbon from benzylchloride can be easily harmonised.

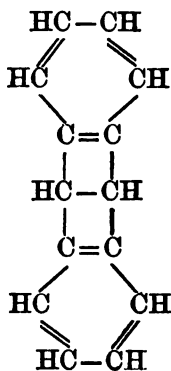
If we assume that, firstly, a molecule of hydrochloric acid is removed from each of the lateral chains, which in conse-

quence attach themselves to each other by two bonds, and that, secondly, the two benzol rings, corresponding to the formation of diphenyl, unite by the loss of two atoms of hydrogen, we arrive at the following structure of anthracen :

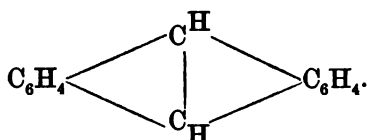


The bonds set free by the removal of the atoms in parenthesis attach themselves, as is easily seen, to each other, so as to form three benzol rings.

The same synthesis, taken in connexion with the circumstance that alizarin yields on oxidation phthalic acid, leads naturally to the following formula, if it is assumed that each methyl group is united by one bond with the benzol-ring of the other benzylchloride, the two lateral chains being simultaneously connected with each other.

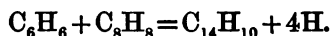


Graebe, and along with him probably all chemists, depending on Van Dorp's synthesis, and on the behaviour of anthracen with soda-lime, have adopted this latter structural formula, as belonging to anthracen. It shows that anthraquinon is not a true quinon, but a double keton. The first formula is recognised as appropriate to phenanthren. The formula for anthracen might be most simply written, thus :

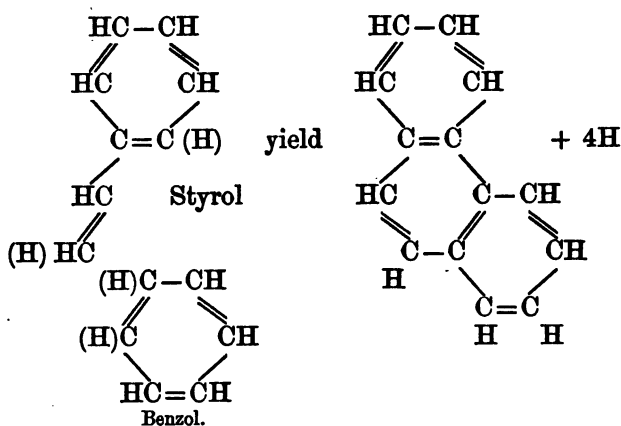


We may here go so far as, depending on the formation of phthalic acid, to resolve the formula more in such a direction that in one at least of the benzol nuclei, the lateral chains have the position 1, 2 ; the formation of alizarin from phthalic acid and pyrocatechin makes this very probable.

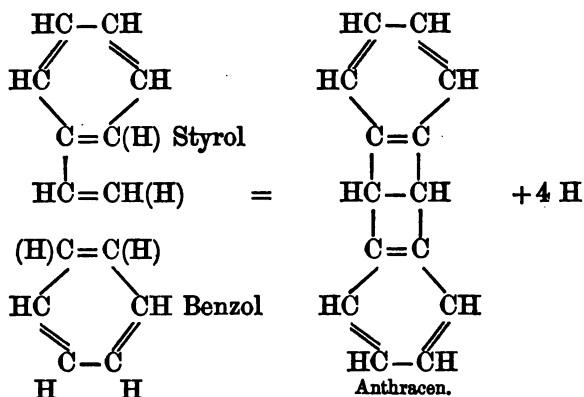
The synthesis of anthracen from styrol and benzol, as discovered by Berthelot, may indeed be more readily explained according to the first formula, but the second formula also throws sufficient light on the progress of the reaction. For this reaction benzol and styrol, when passed through a red-hot tube, would lose four atoms of hydrogen, yielding :



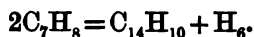
But if we bracket those atoms of hydrogen which are evolved, and suppose that the atoms of carbon are connected by the bonds thus set at liberty, we perceive that a compound may be formed from benzol and styrol, which possesses the first constitution of anthracen.



According to the second formula the reaction would proceed as follows :—



The remaining syntheses observed by Berthelot can all be reduced to the two cases just described; the formation of anthracen from toluol when passed through ignited tubes corresponds to that from benzylchloride—



The synthesis from styrol and benzol can be regarded as

parallel to that from ethylen and benzol, since in this styrol appears as a main product, from which probably the anthracen is afterwards formed.

In its physical properties anthracen much resembles benzol and naphthalin, and forms with these hydrocarbons a series whose members are distinguished by the increment of  $C_4H_2$ . Between the boiling points of the bodies there is an approximately equal distance. Anthracen boils about at the same temperature as mercury. If we therefore take its boiling-point as  $360^\circ$ , we find the following scale of differences :—

|                        | Boiling-point. | Difference. | Melting point. |
|------------------------|----------------|-------------|----------------|
| $C_6H_6$ . . . .       | $80^\circ$     | —           | $6^\circ$      |
| $C_{10}H_8$ . . . .    | $216^\circ$    | $136^\circ$ | $79^\circ$     |
| $C_{14}H_{10}$ . . . . | $360^\circ$    | $144^\circ$ | $213^\circ$    |

The two higher members are strikingly similar as regards their external properties and crystalline character. They form monoclinar crystals closely resembling each other. In their melting-points and solubilities, benzol, naphthalin, and anthracen evince the character of an ascending series. The former rise with the increasing amount of carbon, and the compound becomes less soluble.

The behaviour of the three hydrocarbons with chemical agents is also very similar. None of them yields on oxidation an acid with the same proportion of carbon. They all evince great permanence as regards the chemical arrangement of the atoms of carbon which are not readily torn asunder. But whilst in benzol and naphthalin chinons appear as the characteristic products of oxidation, anthracen under similar circumstances produces a double keton, for as such we must regard anthraquinon, on account of its formation from the benzoate of lime.

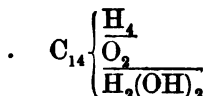
As in benzol and naphthalin, all the hydrogen-atoms of anthracen have a distinct aromatic character; the com-

pounds formed from anthracen by the addition of hydrogen and bromine behave like the corresponding derivatives of benzol and naphthalin. All the considerations, therefore, which go to prove that benzol consists of one closed circle and naphthalin of two, apply also to anthracen, and are opposed to the assumption of saturated or non-saturated lateral chains.

Supported on the assumption founded in the foregoing as to the constitution of anthracen, we may take a further step, and consider the position of the atoms in the substitution-products of anthracen. Alizarin not only yields phthalic acid when oxidised, but can also be obtained from it synthetically. Hence it follows that the two atoms of oxygen must be combined with the two central atoms of carbon, and as alizarin is formed from phthalic acid and pyrocatechin, it further follows that the two hydroxyls are contained in the same benzol nucleus. If the two hydroxyls and the atoms of oxygen are replaced by hydrogen we obtain anthracen, and its formula may then be written simply as follows, the atoms of hydrogen belonging to one and the same circle being written together :—



We have then for alizarin the following formula :—



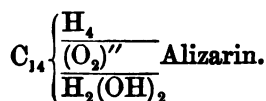
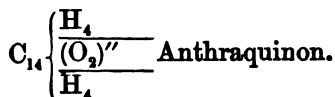
This formula is confirmed by the formation of alizarin from phthalic acid and pyrocatechin, and shows also simply how phthalic and oxalic acids are formed from alizarin. Further, we know that the two hydroxyls assume the position 1, 2, as in pyrocatechin. From this formula for alizarin it follows that also in tetrabromanthracen the four atoms of

bromine take the same position as the atoms of oxygen and the hydroxyls; that therefore two atoms of bromine are connected with the two interior atoms of carbon, and two to the outer ring in the position 1, 2. That the two atoms of oxygen are linked to the interior atoms of carbon is no longer open to doubt, but it may perhaps be of interest to give the reasons which were formerly advanced in favour of this supposition.

Benzol yields on direct oxidation no quinon; from naphthalin naphthaquinon may be with difficulty obtained in a direct manner; from anthracen the derivative in question may be obtained readily. This shows that a larger accumulation of carbon facilitates the formation of quinons. But in anthracen the two atoms of hydrogen belonging to the middle ring are in the greatest degree surrounded by carbon, and the ready formation of anthraquinon is therefore in favour of the above assumption, which is also supported by the great stability of anthraquinon. If the atoms of oxygen were contained in one of the outer nuclei, this would probably be more readily oxidised, and a naphthalin carbonic acid would be obtained. The formation of anthraquinon from bibromanthracen by means of oxidising agents, which do not convert bibrombenzol and bibromnaphthalin into the corresponding quinons, makes it probable that the atoms of bromine replace those atoms of hydrogen which take a peculiar position, and which in a certain manner are more aromatic than those of benzol and naphthalin. If these considerations are accepted, which may be done the more as there is much in their favour and nothing against them, the following formulæ may be assigned to the bromo and quinon derivatives of anthracen:—



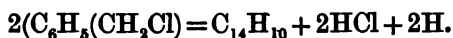




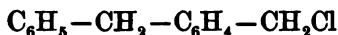
*Preparation and Properties of Anthracen.*

The synthetic methods for the preparation of anthracen have been indicated above.

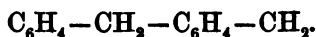
It is obtained, as was stated, on heating benzyl chloride with water to 180° in sealed tubes—



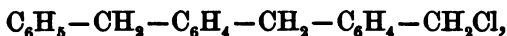
The action of water upon benzylchloride is perfectly analogous to that of zinc upon a mixture of benzylchloride and aromatic hydrocarbons. The water plays, in the first place, an introductory part; the reaction then begins between two molecules of benzylchloride, so that the benzol nucleus of the one molecule loses 1 H, and the other molecule 1 Cl, which both are thrown off as hydrochloric acid, whilst at the same time the chloride



is formed. This latter enters again into reaction in various ways. It may next, losing HCl, become condensed, forming the hydrocarbon—



It may further react with one molecule of benzylchloride in the manner above described, forming a complicated chloride,



which, in turn, again undergoes the same reactions as the chloride of the second degree. There result, therefore, on the one hand, hydrocarbons of the composition  $\text{C}_7\text{H}_8$ , and on the other, chlorides of the composition  $\text{C}_{14}\text{H}_{13}\text{Cl}$ ,  $\text{C}_{21}\text{H}_{19}\text{Cl}$ ,  $\text{C}_{28}\text{H}_{25}\text{Cl}$ , &c.

In the second place, the water, especially at elevated temperatures and on prolonged action, exerts another influence,—it decomposes the chlorides formed, and converts a part of them into the corresponding alcohols and ethers. The ultimate product of the reaction is therefore a mixture of different hydrocarbons, chlorides, alcohols, and ethers, whose molecular weight increases with the duration of the reaction. Besides the chloride,  $\text{C}_{14}\text{H}_{13}\text{Cl}$ , and a hydrocarbon boiling at an elevated temperature, Zincke was unable to obtain any well-characterised compound; but all observations show that the reaction proceeds in the manner indicated above. Zincke became convinced, further, that in the crude product neither anthracen nor benzyltoluol are present, but that both these hydrocarbons are formed during distillation. The manner of their formation, indeed, is so peculiar and complicated, that it could not be discovered theoretically. Anthracen is formed on the distillation of its principal quantity, but decidedly only in the second place. It is no direct product of decomposition, but owes its formation to a previously formed and very complicated hydrocarbon, which is split up under the influence of heat into anthracen and other hydrocarbons. Benzyltoluol, on the other hand, is a direct product of decomposition, and is especially formed from the chloride,  $\text{C}_{14}\text{H}_{13}\text{Cl}$ , which is resolved into hydrochloric acid, benzylchloride, benzyltoluol, and hydrocarbons of high molecular weight; in small quantities it also seems

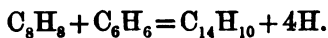
to be formed, along with anthracen, during the decomposition of the latter. The entire process of formation of anthracen and benzyltoluol from benzylchloride may be represented as follows:—When benzylchloride is heated with water there are formed the bodies mentioned above, among which the chloride,  $C_{14}H_{13}Cl$ , which boils in a vacuum at  $204^{\circ}$ – $206^{\circ}$  with partial decomposition, and hydrocarbons with a high boiling-point (from  $280^{\circ}$  to above  $300^{\circ}$  in a vacuum) predominate, whilst oxygenous bodies are only present to a small extent. On the distillation of these crude bodies, which in all cases should be freed from undecomposed benzyl chloride by means of a current of steam, there appear, if they are heated under ordinary atmospheric pressure, principally hydrochloric acid, water, benzylchloride, benzyltoluol, and resinous or tarry hydrocarbons, which on further heating yield anthracen and toluol, along with small quantities of other bodies. A small portion of the resinous or tarry hydrocarbons, which yield on decomposition anthracen, is possibly already present in the crude product. In any case, the latter approach the hydrocarbons formed directly from benzyl chloride. Like these, they correspond to the formula  $nC_7H_6$ , and are only distinguished by their molecular weight. The decompositions above described may be traced very accurately in a vacuum, where the decomposition of the chloride  $C_{14}H_{13}Cl$  is less energetic, the formation of hydrochloric acid is less prominent; but water and benzylchloride with benzyltoluol, as well as the resinous hydrocarbons, are plentifully formed. The latter are generally obtained as solid masses, resembling colophonium, which melt below  $100^{\circ}$ , giving off a pleasant aromatic odour. In a vacuum they boil without decomposition, but if heated under atmospheric pressure they are split up into anthracen and toluol.

The chloride  $C_{14}H_{13}Cl$ , as obtained by Zincke on distillation in vacuum, manifests similar phenomena of decomposition; if heated under atmospheric pressure, it yields hydro-

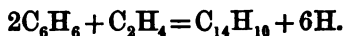
chloric acid, benzylchloride, benzyltoluol, and a residue which afterwards yields anthracen and toluol. If the chloride is distilled in a vacuum, the same decomposition ensues, though slowly. A portion distils undecomposed, but the greater part is decomposed as above described, so that on each successive rectification of the chloride larger proportions of the resinous hydrocarbons are obtained, which in turn naturally yield anthracen and toluol. Various other bodies are also formed in small quantities on the distillation of the crude product; amongst others a hydrocarbon, which boils in vacuum at a pressure of 20 to 30 mm., at  $264^{\circ}$ – $267^{\circ}$ ; further, very small quantities of a solid hydrocarbon, which melts at a low temperature, also small quantities of oil of bitter almonds and anthraquinon, both which are to be regarded as decomposition-products of oxygenated bodies formed from benzylchloride.

Anthracen, therefore, as evidently appears from these experiments, is simply a product of the splitting up of a higher hydrocarbon, probably of the formula  $nC_7H_8$ .

Similar splittings-up are manifested of the higher hydrocarbons, which are formed, along with benzylchloride and benzyltoluol, by the action of zinc upon mixtures of benzol or toluol with benzylchloride; they are generally resolved with little loss into anthracen or toluol. The technological observations made concerning the preparation of anthracen from coal-tar go to prove that this hydrocarbon is not contained as such in the tar, but is formed during distillation. Probably many of the bodies obtained from tar owe their origin to similar decompositions of higher hydrocarbons. It must, however, be here admitted that some chemists assume the pre-existence of anthracen in the tar, and maintain that they have ascertained its presence by analysis. Anthracen is also formed by heating styrol with benzol,



or by heating benzol with ethylen,



The latter mode of formation supports the second formula proposed by Graebe and Liebermann.

Anthracen, however, is most readily formed from those parts of coal-tar which boil at the highest temperature, of which, according to Crace Calvert, it forms only 1 per cent. According to M. Reimann, the tarry oils from the Swabian (?) lias-slate are rich in anthracen. According to Crace Calvert, it seems to be formed, or at least liberated, in the last part of the process. If the distillation is only carried so far that a very soft pitch remains, the oils obtained yield little or no anthracen. If the distillation is pushed so far as to produce 10 or 15 per cent. more oil, a hard pitch remains, of little or no value; whilst the anthracen obtained, according to the nature of the coal, may amount to from  $1\frac{1}{2}$  to 8 per cent. of the heaviest oils. It is scarcely remunerative to deteriorate the quality of the pitch for the sake of securing it. Its separation from the heavy oils and its purification are very tedious. The purest product which Calvert was able to obtain on a moderately large scale, contained 40 per cent. of anthracen if cold-pressed, and 70 per cent. if hot-pressed. Its preparation is embarrassed by the circumstance that at moderate temperatures anthracen very readily dissolves in its homologues; thus, e.g. at  $40^\circ$  to  $50^\circ$  an oil yields on filtration a relatively large amount of anthracen, which at  $70^\circ$  to  $80^\circ$  is completely dissolved.

The manufacture of anthracen from coal-tar is conducted as follows:

If the coal-tar is distilled in the usual manner, it yields on the average per ton (=1,000 kilos. or 900 litres) about 13-14 litres (=455 to 490 fluid ounces) of ammoniacal liquor, 29 to 30 litres (=1,015 to 1,050 fl. oz.) of very light oils containing benzol, 90 to 100 litres (3,150 to 3,500 fl. oz.)

of light oils still containing a little benzol, and fit for use as lamp-naphtha.

If the process is broken off at this juncture, there remains in the still the so-called asphalt, a black mass, semi-liquid even when cold, and consisting of heavy oils and of pitch. If, on the contrary, the distillation is continued, as is commonly done, from 300–312 litres (10,500 to 10,920 fl. oz.) of heavy oils, so-called creosote-oils, are obtained. The residue in the still is then fluid enough to be run off when hot; but on cooling it congeals to a black, shining, brittle, solid mass, 'hard pitch,' which softens only at high temperatures, and which even in summer can be carried in open carts without packages.

In many cases the distillation is only pushed so far as to yield 190 to 200 litres of the heavy oils. The residue is then 'soft pitch,' an intermediate step between asphalt and hard pitch. At ordinary temperatures it is solid and hard, though less brittle than the 'hard pitch,' and somewhat flexible. At slightly elevated temperatures it becomes soft and plastic like wax, and in the heat of summer it melts, and can therefore be transported unpacked in open carts only in winter.

The heavy oils consist of liquid oily hydrocarbons, naphthalin, phenol, cresol, and similar products, and contain also more or less anthracen. On account of the separation of naphthalin and anthracen at reduced temperatures, they have often a butter-like, smeary consistence; their colour is at first yellow or yellowish-green, but on exposure to the air passes gradually into a brown, which constantly grows darker.

The distillation of the heavy oils, especially if it is intended to obtain lubricants and anthracen, may be appropriately divided into two or three periods. The substances most valuable as lubricants, naphthalin, cresol, and phenol, are relatively the most volatile, and pass over first. Anthracen

does not appear till the last period of the process. The phenomena observed during this fractionated distillation are as follows :—

The distillate first passing over, if a small sample is allowed to cool in a flat vessel, is found to deposit naphthalin in crystals. So long as this takes place, the oil is collected separately, and used for the impregnation and preservation of wood, for which purpose it is peculiarly fitted, on account of its high percentage of phenol (carbolic acid).

When the distillate remains fluid on cooling, it is collected in another receiver, and used as a liquid lubricant.

After a time the distillate, on cooling, no longer remains fluid, but assumes a thick, paste-like consistence, due to the deposition of paraffin. This product, the so-called 'green grease,' containing heavy oils, naphthalin, phenanthren, and anthracen, is the principal material for the manufacture of anthracen, and is, according to J. Gessert, most conveniently worked up in the following manner : The paste-like mass is first 'whizzed' in a centrifugal machine. The residue, still containing many oils, is heated to about 40° C., and introduced into powerful hydraulic presses, which, if practicable, are fitted with hot plates in the style of oil presses. In this manner the greater part of the oils is removed, leaving a cake rich in anthracen. The filter-press may also be very advantageously used for preparing crude anthracen. The paste-like mass, heated to 30°–40°, is pumped into the filter-press, which may be conveniently combined with the hydraulic press, and thus a crude product, rich in anthracen, is at once obtained. The use of the filter-press is particularly to be recommended in the treatment of oils containing but little anthracen, and which are too mobile to be introduced into the centrifugal machine.

E. Kopp has carefully studied the preparation of anthracen from coal-tar, and especially from soft pitch, and has arrived at the following results. The distillation of the tar

should be pushed only to the point when the white naphthalin and the phenol have passed over, and the heavy oils are still liquid; 120 to 150 litres of heavy oil may, therefore, be obtained per ton. These contain mere traces of anthracen, the bulk of which remains behind in the soft pitch.

In this soft pitch, obtained from the gas-works of Turin, Kopp found considerable quantities of anthracen (4 to 6 per cent.). At the present price of this article it would be remunerative to sacrifice the pitch, in order to extract from it the anthracen and certain other products. To obtain the largest possible yield of anthracen from this soft pitch, certain precautions are absolutely necessary.

The still must be greater in breadth than in depth, and the distillation must not be carried on too rapidly. The pipe for the exit of the vapours must be of a large size, and must open into the still only  $1\frac{1}{2}$  to 2 decimetres above the surface of the boiling pitch, and then bend immediately downwards, so that the heavy vapours scarcely require to rise, but may flow easily out, and at once sink downwards. The condensing-water must be very warm even at the outset, and must subsequently be kept boiling. Towards the end of the process the efflux of the vapours must be promoted by a current of superheated steam or of gas. A current of steam has the advantage as compared with gas that, being in itself capable of condensation, it does not interfere with the condensation of the vapours of the heavy hydrocarbons. Still these vapours condense so readily that a current of gas, if not too violent, is not injurious.

As a current of gas we may use atmospheric air; or better still, in order to avoid every risk of conflagration or explosion, a mixture of carbonic oxide and nitrogen. This mixture is obtained by passing air through a stove, or a red-hot iron tube, filled with wood charcoal.

The distillation of the soft pitch is conducted as follows: The iron still (for operations on a scale not too large) is filled



with melted pitch, heat being at once applied. As soon as distillation begins, the fire is moderated, in order to obviate boiling over, which, however, does not readily occur. When a certain quantity of heavy oil has passed over, an equal volume of melted pitch is introduced through a vertical tube, which passes through the dome of the still, and dips into the boiling pitch to half its depth, and which is capable of being opened and stoppered. In this manner the level of the pitch within the still is kept nearly constant. Thus as much more pitch is gradually introduced as the still originally contained. At the same time the superheated steam and the current of air deprived of its free oxygen are caused to sweep directly over the surface of the boiling pitch, or are even conducted into it. In this manner the vapours of anthracen are mechanically swept away, and condense partly in a fused state, but partly as a crystalline sublimate.

The still is not to be heated too violently, lest the pitch should burn on its bottom, and lest it should be difficult to observe the progress of the operation. Great care must be taken that too much orange vapour of chrysen, pyren, and benzerythen does not pass over, which would greatly complicate the subsequent purification of the anthracen. Towards the end of the process the distillation may be regarded as sublimation.

In most cases the residue in the still is sufficiently liquid to be run off, whilst hot, in the ordinary manner.

If it is too thick to flow off, it is not difficult to arrange the whole apparatus so that the neck of the still can be closed, and thus a pressure of  $\frac{1}{4}$  to  $\frac{1}{2}$  an atmosphere can be produced in the body by the influx of steam or air, which greatly assists in the escape of the pitch.

If it were desired to heat the pitch till carbonised, this could not be done in an iron still, partly from the difficulty of subsequently extracting the charred mass, and partly because the iron would be quickly worn out and destroyed.

It is therefore better to use either fire-clay retorts, like gas-retorts, or still better muffle-furnaces, which latter are not only less costly, but admit of the treatment of larger quantities at once.

These furnaces consist of an arch rising from a hearth, under which the fire is conducted. Such a furnace may be five metres in length, two in breadth, and the same in height to the crown of the arch. The fire-box is placed under one of the ends of the arched space, and the flues range backwards and forwards in the direction of the sides, and are conducted on the opposite end into a main flue leading to the chimney. The man-hole is also in one of the ends, and is walled up before the fire is kindled, a cast-iron frame with sliding doors having been first fixed in.

In the middle of the furnace vault there is a round aperture through which the furnace is charged with pitch; and which is then again carefully closed.

The pitch can be introduced either in blocks, or in a liquid state. In the latter case it is melted in a large iron tank fixed above the furnace, and heated by the hot air passing through the flues before entering the chimney. If needful, the pitch may be melted over a separate fire. Near the crown of the arch, in the flat, vertical end-wall, opposite the fire-box, there is a moderately large round aperture in which is fixed an iron pipe, to conduct away the condensing vapours. If the pipe is sufficiently long the condensation is effected by contact with the air, but a shorter pipe may be used if water is applied, hot at first and afterwards boiling. A branch pipe leads the uncondensed vapours and combustible gases into the fire-box, where they are consumed.

Towards the end of the operation, which may be known by the condensation-pipe growing cold, the fire is allowed to go out. Some time afterwards the above-mentioned iron sliding door is cautiously opened, after a part of the brick-work has been removed, and the condensation-pipe has been

closed. The dense vapours in the interior of the furnace catch fire and burn. Without this precaution the residual coke would still contain pitchy particles, which by the arrangement just described are burnt away, leaving the coke quite pure. When the vapours are consumed, the fire in the interior of the furnace expires, as the access of air is insufficient for the combustion of the coke. The man-hole is then entirely broken open; the coke, still glowing, is extracted and quenched with water. It yields a fine, hard, porous product, almost free from sulphur compounds and from ash, and finds a variety of useful applications.

On account of the difficulty encountered in working up anthracen contaminated with pyren, chrysen, and other hydrocarbons, boiling at high temperatures, it will always be necessary to submit the oils obtained from the carbonisation of the pitch to re-distillation and rectification.

Since even pure anthracen is partially decomposed on distillation, the process must be conducted with the aid of a current of superheated steam, or of hot gas freed from oxygen, and the operation must be broken off as soon as the above-mentioned less volatile hydrocarbons begin to distil over.

The temperature of  $360^{\circ}$ – $380^{\circ}$  should not be exceeded, and towards the end of the process the distillation becomes a true sublimation, the anthracen escaping not as a liquid, but as a powder—sometimes even crystalline.

According to whichever method the crude, smeary, thick-flowing anthraceniferous mass has been obtained, it must be submitted to a process of purification, depending mainly on the following principles:—

1. Leaving the heavy oils for some days in a cool place, that the anthracen may be deposited as completely as possible.
2. Filtration, preferably by a filter-press, to separate the liquids from the solids. If it is simply filtered, as is often

necessary, the centrifugal machine may be used before the first pressing.

3. Pressing the mass twice after removal from the centrifugals; the first time cold, the second time with the simultaneous application of a temperature of 30°, 40°, or even 50°. The pressure must be applied with great care, a very powerful hydraulic press being preferably employed. The oils obtained on pressing often yield, if allowed to settle in a cool place, a small further amount of anthracen. After pressure the mass should be perfectly dry, readily friable and capable of being sifted.

4. Washing the finely-ground product with benzol, light petroleum oils, ligroin, &c. The light, volatile benzines and naphthenes readily dissolve the liquid oils, naphthalin, phenol, &c., without at the same time dissolving appreciable quantities of anthracen. If the lixiviation takes place at a boiling heat, which is often preferable, the anthracen dissolved by the benzol or petroleum naphtha is re-deposited as the solvent cools.

5. The lixivated anthracen is then placed in a centrifugal machine, or strongly pressed, and is removed to the drying-room.

For the purification of anthracen the most varied means have been proposed. It is recommended to be treated with solvents, sometimes cold and sometimes hot. Some propose alcohol or ligroin, others benzol, naphtha, or even bisulphide of carbon. Some of these detergents are very unpractical, either on account of their high price, their volatility, or from their power of dissolving too much anthracen.

Thus, at common temperatures:—

|                          |   |                         |
|--------------------------|---|-------------------------|
| 100 parts alcohol .      | . | dissolve 0·6 anthracen. |
| „ benzol .               | . | „ 0·9 „                 |
| „ bisulphide of carbon „ | „ | 1·7 „                   |

These determinations of solubility refer to chemically pure

anthracen, but if it is contaminated with various other low hydrocarbons, as is the case with crude anthracen, its solubility in the above-mentioned purifying agents is considerably increased. Alcohol and bisulphide of carbon must be at once rejected, on account of their high price and their great volatility. Ligroin is cheap, but does not work well. Benzol is too dear. The best purifying agent is heavy naphtha, the so-called 'solvent naphtha,' a mixture of the higher hydrocarbons, which begins to boil about 120° C. The method of purification to be adopted depends on the percentage of pure anthracen in the crude sample. A determination of anthraquinon is first made according to the method described below, and the crude anthracen is then divided into two classes, such as contain less than 25 per cent. of real anthracen, and such as contain more.

The former kind is first treated in the cold with about 25 per cent. of naphtha in an iron washing-apparatus, consisting of cylinders fitted with mechanical agitators. The anthracen and the naphtha are introduced, the agitator is set in motion, and the mixture is stirred for twenty-four hours. The whole is then thrown upon a filter, which is made as air-tight as possible, in order to prevent the evaporation of the naphtha, and the solvent is removed either by atmospheric pressure or by the application of a vacuum. The naphtha which drains away is distilled off, the residue left in the still is let off whilst hot, and after cooling subjected to hydraulic pressure, and further treated like crude anthracen. The anthracen taken from the filter, once washed, is exposed to very strong hydraulic pressure, and contains then from 30 to 35 per cent. of anthracen. The pressed cakes are ground and treated exactly like crude anthracen, containing more than 25 per cent. of actual anthracen.

Anthracen containing from 25 to 50 per cent. of actual anthracen, is ground fine, sifted, and then placed in the washing cylinder, with an equal weight of naphtha, and

stirred. The longer it is washed the better. Heat is not necessary, since cold naphtha purifies the anthracen very well if the action is sufficiently prolonged. The main point is that the crude anthracen must be ground as fine as possible, and that all its particles must be brought in contact with the naphtha. If the operation is properly conducted, the anthracen diffused in the naphtha is obtained in the state of an impalpable powder. The mixture of anthracen and naphtha is then placed on a filter as above directed, the naphtha removed as far as possible by atmospheric pressure, or by means of a vacuum, and the anthracen remaining on the filter pressed as strongly as possible in the hydraulic press. The cakes thus obtained are dried, the filtrate of naphtha is distilled, and the residue left in the still is treated like a crude anthracen of a low percentage. The oils last obtained may either be burnt, by driving them under the steam boiler by means of a jet of steam, or they may be used to saturate wood, as a coarse paint, &c. The following arrangement is very suitable for burning the oils. They are placed in an old boiler, which in severe weather may be heated so as to keep the contents liquid. At the bottom of the boiler a pipe is fixed to let off the oil, capable of being opened and closed by means of a cock. This pipe leads under the steam-boiler, and is beaten out wide at its extremity. Within this pipe there is another one, as in the tubes of a blowpipe-lamp,<sup>1</sup> which conveys steam from the steam-boiler. If it is desired to heat the boiler, there must naturally be a certain amount of internal tension. If the cock of the oil-boiler and that of the steam-boiler are simultaneously opened, the steam rushing out of the steam-pipe into the oil-pipe, converts the oil into an extremely fine dust, which, when kindled, heats very well.

The anthracen cakes, obtained as above directed, must be comminuted as finely as possible preparatory to further

<sup>1</sup> E.g. in Herapath's gas blow-pipe.

treatment. This minute subdivision cannot be effected by grinding and sifting, the best expedient being sublimation. Anthracen at above 50 per cent. may be sublimed directly. The sublimation is performed either by means of air deprived of its oxygen by a passage over ignited charcoal, or of superheated steam. The apparatus employed may be either retorts or boilers. In this manner the anthracen is obtained in fine white laminae,—the most suitable state for oxidation into anthraquinon. The process of sublimation cannot, however, be regarded as a means of purification, since most of the foreign hydrocarbons are volatilised simultaneously. Sublimation, therefore, is merely a means of comminution.

Instead of washing the anthracen another method has been applied in some establishments, although with very unsatisfactory results. The anthracen is mixed with caustic potash and a little lime, and distilled in retorts shaped exactly like gas retorts. Each retort is charged with 200 kilos. anthracen, no matter of what percentage, 60 kilos. of Montreal potash, and 12 kilos. lime. The anthracen is previously ground up with the potash and the lime. A strong odour of ammonia is often perceived, and if the mixture is lixiviated with water a green solution is obtained which deposits greenish blue flocks of an exceedingly unpleasant odour. After distillation there remains in the retort a wax-like substance which takes fire on exposure to the air, and deposits on colder parts a white sublimate of carbazol. The distillate of anthracen forms solid yellow pieces, containing about 40 per cent. of pure anthracen. Caustic soda cannot be employed on account of its difficult fusibility, and as caustic potash melts too readily a little lime is added. The caustic potash can be recovered from the residue in the retort by lixiviation and boiling with lime. Distillation with caustic potash is said to destroy the chrysen present; but this destruction extends also to the anthracen, as may be

seen from the following figures :—600 kilos. anthracen at 31 per cent. of pure anthracen were distilled with 180 kilos. potash and 36 kilos. lime. The yield was 383 kilos. of anthracen at 44 per cent. The loss was therefore 17·5 kilos., or 10 per cent. If we include the considerable consumption of fuel required in heating the retorts, we see at once that this method of purification is the most costly known. Anthracen purified in this manner is, however, the best material for the preparation of chemically pure anthracen. It is merely requisite to wash the distillate of anthracen once with bisulphide of carbon, and to recrystallise several times from petroleum and benzol, in order to obtain splendid white crystalline laminæ with a blue fluorescence. To prepare from the ordinary crude anthracen chemically pure anthracen with a blue fluorescence, is one of the most difficult tasks. The yellow colouring matters are so difficult to remove, and adhere so obstinately to the crystals, that it is scarcely possible to obtain a specimen of a higher percentage than 90. To obtain pure anthracen it is preferable to sublime at the lowest possible temperature and to wash subsequently with ether, which dissolves the adherent yellow substances. Or the anthracen may be dissolved in benzol, and the solution may be bleached by exposure to sunlight.

In the latter case anthracen separates out on cooling in colourless crystals, possessing the splendid blue fluorescence, described by Fritzsche. Still the anthracen purified in this manner contains an admixture of para-anthracen. The best way of obtaining anthracen is the reduction of its derivatives with zinc powder.

Drs. Greiff and Versmann have proposed to distil anthracen from pitch, but the quality thus obtained, the so-called 'pitch anthracen,' is exceedingly difficult to treat. By distillation with potash it is said to be possible to ascertain whether a given sample is tar or pitch anthracen. The



former is said to lose nothing by this process, whilst pitch anthracen sustains a loss.

To determine the value of a crude anthracen the most various processes have been employed. Alcohol, petroleum spirit, sulphide of carbon, or a mixture of both have been used to remove the foreign substances present. All such methods of analysis have now been given up in favour of the determination of anthracen as anthraquinon, as proposed by Luck—the only accurate and rational method.

As it may, however, be of historical interest to know the earlier processes for the determination of anthracen, we mention the principal methods formerly in use.

1. *Alcohol process.*—20 grms. anthracen are heated to a boil with 100 c.c. of alcohol at 98 per cent., allowed to cool, filtered on a weighed filter, and washed with alcohol till the filtrate amounts to 300 c.c. The residue on the filter is then dried at 100° C., weighed, and after deducting the weight of the paper, calculated as pure anthracen. According to Faust, 20 grms. of anthracen are treated with 150 c.c. of boiling alcohol at 95 per cent.; cooled down to 15.5° C., washed with 250 c.c. alcohol, dried at 100° C., and weighed. In order to test this so-called pure anthracen for foreign insoluble bodies, 5 grms. are taken and boiled till all the anthracen is dissolved, and the liquid is filtered whilst boiling. The residue is further washed with boiling alcohol, and the portion insoluble in this liquid—which if above 1 per cent. is a sophistication—is deducted from the percentage obtained.

2. *Petroleum and bisulphide of carbon process.* *Perkin's method.*—50 grms. anthracen are rubbed up with 10 ozs. petroleum spirit of spec. grav. 0.740, and filtered through a linen filter, the vessel being rinsed out and the residue washed with 20 ozs. more. The filter is first pressed with the hand, and then between iron plates in a screw-press. The residue is powdered, introduced into a bottle holding 6 to 7 ozs.,

and strongly shaken for two or three minutes with 5 ozs. bisulphide of carbon. It is then thrown on a balanced filter, pressed between folds of filter-paper, and then dried and weighed. After deducting the filter the residue is the amount of pure anthracen. The anthracen thus obtained must have a melting-point not below  $200^{\circ}$  C. and not above  $212^{\circ}$  C., taking as the melting-point the mean between the beginning of melting and the beginning of congelation.

3. *Cohn's bisulphide of carbon method.*—10 grms. crude anthracen are agitated for two hours in a flask with 30 grms. of bisulphide of carbon, thrown on a weighed filter and washed with 30 grms.  $\text{CS}_2$ , the last third part of which is poured upon the filter three times. The residue is then pressed between folds of filter-paper, dried, and weighed.

According to Déhaynin, 20 grms. of anthracen are heated in a flask with 40 c.c. bisulphide of carbon for twenty minutes with constant agitation, allowed to cool down to  $15^{\circ}$  C., filtered on a weighed filter, and washed with so much bisulphide of carbon that the filtrate amounts to 100 c.c. It is then dried and weighed, and the residue taken as pure anthracen. The latter methods with petroleum and bisulphide of carbon, and with bisulphide of carbon alone, have remained longest in use, although it is not possible to obtain with them exact results, since chrysen, one of the most frequent accompaniments of anthracen, dissolves in bisulphide of carbon only with extreme difficulty, and it is therefore very possible, after treatment with this solvent, to obtain a product which has the right melting-point, but which is still not anthracen.

F. H. Davis has made comparative investigations with anthracen according to the alcohol, the bisulphide of carbon method, and the process of Luck, to be described below, and concludes from his results that the two former methods are to be rejected. In case of crude anthracens, containing from

12 to 34 per cent. of the pure article, the results of Luck's method and of the sulphide of carbon process agree approximately, but in case of richer samples the latter method yields invariably exaggerated results.

The alcohol method has this defect, that the alcohol dissolves a certain quantity of anthracen, whilst it does not remove any chrysen which may be present. The weight of the latter may, indeed, to a certain extent compensate for the loss due to the solubility of the anthracen in alcohol, but an accurate determination of the proportion of pure anthracen cannot be looked for by this process.

The bisulphide of carbon method is probably still less accurate than the alcohol process, since bisulphide of carbon dissolves about 2 per cent. of anthracen, and its evaporation inevitably takes place in a varying degree when the operation is performed by different chemists. Instances have come under the observation of Davis, when two chemists examining one and the same sample of anthracen by this method obtained results varying to the extent of 4 to 6 per cent. Discrepancies of 2 to 3 per cent. occur frequently both with this method and with the alcohol process.

The results which Davis obtained on comparing the three methods are as follows:—One and the same crude anthracen gave with alcohol of 0.825 spec. grav. (89 per cent.) 34.645 per cent. of insoluble matter, with the melting-point  $187.5^{\circ}$  C. With bisulphide of carbon the yield was 23.250 per cent., melting-point  $198.2^{\circ}$  C.; and by oxidation to anthrachinon 28.358 per cent. of pure anthracen.

Lucas has also compared the determination of anthracen by Luck's process with the bisulphide of carbon analysis, and has tabulated his results. From twenty samples of crude anthracen procured from eight different English manufactories he obtained the following figures:—

*Percentage of Pure Anthracen.*

| No. | By the Bisulphide of Carbon process | By conversion into Anthraquinon | Difference |
|-----|-------------------------------------|---------------------------------|------------|
| 1   | 9.20                                | 11.90                           | + 2.70     |
| 2   | 16.00                               | 16.40                           | + 0.40     |
| 3   | 24.50                               | 26.10                           | + 1.60     |
| 4   | 34.00                               | 27.80                           | - 6.20     |
| 5   | 35.00                               | 28.20                           | - 6.80     |
| 6   | 38.00                               | 29.67                           | 8.33       |
| 7   | 38.00                               | 33.38                           | 4.62       |
| 8   | 40.50                               | 38.00                           | 2.50       |
| 9   | 43.00                               | 33.80                           | 9.20       |
| 10  | 49.00                               | 34.24                           | 14.76      |
| 11  | 57.40                               | 44.51                           | 12.89      |
| 12  | 58.00                               | 41.50                           | 16.50      |
| 13  | 59.00                               | 44.51                           | 14.49      |
| 14  | 59.50                               | 39.37                           | 20.13      |
| 15  | 60.00                               | 37.66                           | 22.34      |
| 16  | 60.00                               | 42.80                           | 17.20      |
| 17  | 64.12                               | 48.79                           | 15.23      |
| 18  | 65.00                               | 47.08                           | 17.92      |
| 19  | 67.00                               | 46.22                           | 20.78      |
| 20  | 73.00                               | 49.22                           | 23.78      |

From these experiments it follows that the anthraquinon method alone gives correct results, and that the product obtained with bisulphide of carbon is by no means pure anthracen.

The anthraquinon process has also undergone several modifications and improvements before it could be regarded as satisfactory. Certain important points required a closer investigation before Luck could even make his process known. It had to be ascertained whether a given quantity of pure anthracen on oxidation with glacial acetic acid and chromic acid would yield the amount of anthraquinon which theory requires; whether the latter compound on prolonged contact with chromic acid might not pass into a higher stage of oxidation; and lastly, how the bodies which naturally accompany anthracen, or which are accidentally or purposely mixed with it, might behave on oxidation with chromic acid.

The results obtained by Luck were as follows :—

1. Pure anthracen yields exactly the theoretical amount

of anthraquinon when dissolved in glacial acetic acid and treated at a boil with 3 to 4 parts of chromic acid. Instead of 100 he obtained 99·4 per cent.

2. Pure anthraquinon dissolved in acetic acid along with 3 to 4 parts of chromic acid was boiled gently for two hours, and yielded on dilution with water the original quantity of anthraquinon. Taken 0·447 grm., recovered 0·446 grm.

3. The compounds accompanying or contaminating anthracen, on sufficiently prolonged oxidation with chromic acid, are all converted into acids or into bodies soluble in alkaline liquids, and can thus be separated from anthraquinon. This applies equally to phenanthren, chrysen, &c., and to paraffin and the so-called empyreumatic resins, &c. In reliance upon the above observations, Luck gave his process the following form :—

One grm. of the anthracen in question is dissolved at a boiling heat in 45 c.c. glacial acetic acid in a small flask. It is filtered, if necessary, at a boil through a small filter, and a solution of 10 grms. chromic acid in 5 c.c. water and 5 c.c. glacial acetic acid is gradually added in small portions, so that the liquid may not cease to boil gently. This is continued until a distinct and permanent greenish yellow colour appears, or till, after prolonged boiling, a drop of the liquid placed upon a clean silver coin produces in a few minutes a reddish spot of chromate of silver. The liquid is then allowed to cool, gradually diluted with 150 c.c. water, filtered after a few hours, and the anthraquinon on the filter is washed first with water, then with hot, very dilute potash lye, then again with water, and dried at 100° C. After weighing, the anthraquinon is quickly removed from the filter, the latter is weighed again, and its weight is deducted from the gross amount of the anthraquinon. To the nett weight thus obtained 0·01 grm. is added, because, according to Luck's experiments, if 50 c.c. glacial acetic acid and 150

c.c. water have been used as above directed, exactly 10 milligrms. anthraquinon remain in solution in the filtrate.

Commercial chromic acid frequently contains lead. If this is the case, the anthraquinon, after having been washed with water and alkali, must be treated with a hot solution of acetate of ammonia. Some time after this method of analysis was published, it was found that the results obtained were incorrect, since a part of the impurities was not perfectly oxidised, and was thus estimated as anthraquinon. Luck therefore made known a further method, according to which the anthraquinon obtained, after washing with alkali, is treated with permanganate of potash in an alkaline solution. In the performance of this process the anthraquinon, after treatment with alkali, is washed with the washing-bottle into a beaker or a small capsule, rendered very feebly alkaline, and brought to a boil. A solution of permanganate is now added drop by drop until it is no longer reduced, and a red colour appears instead of the green. A little oxalic acid and sulphuric acid are then added to reduce the excess of permanganate, and to dissolve the peroxide of manganese formed. It is then filtered through the same filter, washed with water till the acid reaction has disappeared, then with very dilute boiling soda lye, and then again with water. It is dried at 100° C., and weighed as above. Luck states also that for many samples of anthracen as much as 15 grms. of chromic acid are needful. He writes: 'In general 10 grms. of chromic acid may suffice, but in certain cases 15 may be required for perfect oxidation.' This leaving open the amount of chromic acid to be used leads often to very unpleasant results. Thus, e.g., a crude anthracen was oxidised with 10 grms. of chromic acid, and the result obtained in four analyses was each time 26 per cent., whilst the same anthracen, on treatment with 15 grms. of chromic acid, gave in six analyses 23 per cent. of anthracen, and in both cases chromic acid was present in excess. It seems that a slight

excess of chromic acid has no longer an oxidising action upon the anthracen in presence of the acetate of chrome, and that a larger excess of chromic acid completes the reaction. Luck, and before him Graebe and Liebermann, have shown that chromic acid, and indeed oxidising agents in general, have no further action upon anthraquinon. As 15 grms. of chromic acid suffice in all cases for the oxidation of 1 grm. of anthracen, it would be advisable always to use the higher number, and to adopt it as a standard in all contracts for anthracen. When only 10 grms. of chromic acid are employed, it may often happen that after boiling for three to four hours an excess of free acid may be present, and yet the substance may not be perfectly oxidised. The most careful analyst may thus make costly mistakes, and the door is opened wide for 'buyers' and 'sellers' analyses. The duration of the oxidation is of no importance; three to four hours are sufficient, and six to eight hours do not modify the result. An objection to Luck's method is the hot filtration which has to be performed when necessary. If organic bodies are present, insoluble in acetic acid, they are destroyed during the oxidation. If inorganic bodies occur, they consist of non-volatile matter—sand, &c.—and are best determined by the incineration of a weighed portion of crude anthracen. If it is desired to determine the insoluble constituents by means of acetic acid, it is every way more accurate to extract a portion of crude anthracen perfectly with acetic acid, than to filter the solution destined for the analysis whilst hot, and thus to lose anthracen by the evaporation of the acid and by crystallisation in the filter.

The process of Luck, with the additional precautions as above described, is the only method now in use. Still, the anthraquinon thus obtained is not quite pure. Anthraquinon is well known to have the property of dissolving in sulphuric acid, but it is only converted into sulphacids at temperatures far above 200° C. With the impurities the case is different.

Chrysoquinon becomes at  $100^{\circ}$  C. an indigo-blue sulphacid, which turns brown on the addition of water. The same change takes place with the other hydrocarbons, or products of oxidation. If we take an anthraquinon which has undergone Luck's subsidiary process, and heat it with concentrated sulphuric acid to  $100^{\circ}$ – $110^{\circ}$  C., the acid becomes either at once brown, or takes a blue, which turns yellow on dilution with water. Or, even if the sulphuric acid decanted from the anthraquinon is colourless, a coloured solution is subsequently obtained on extracting the anthraquinon with a dilute lye of potassa. Since anthraquinon is neither sulphated by sulphuric acid at a temperature below  $200^{\circ}$  C. nor dissolved by dilute alkaline lyes, it follows that the bodies removed by sulphuric acid must be impurities which have resisted the permanganate. In fact, the results of Luck's method, followed up by the use of permanganate and those of the sulphuric acid process, vary respectively from 1 to 8 per cent.

If we wish to use the latter method, we conduct the oxidation exactly as prescribed by Luck, and re-oxidise with permanganate (which, however, is not absolutely necessary), dry, and dissolve the anthraquinon obtained from 1 grm. anthracen in 10 grms. of pure sulphuric acid, free from lead. For this purpose the anthraquinon may be conveniently placed upon a large flat watch-glass, the sulphuric acid added, and the whole heated in the water-bath, or better, to  $112^{\circ}$  C. in the air-bath, for ten minutes.

It is then allowed to cool, when the anthraquinon crystallises out, diluted with much water, boiled, let cool, and filtered. It is next washed with water till the reaction of the washings is perfectly neutral, then with dilute soda lye, then again with water, dried and weighed. Of course the 0.01 grm. of anthraquinon dissolved in acetic acid must here be taken into account. The anthraquinon thus obtained



undergoes no loss, whether by oxidation or by repeated treatment with sulphuric acid, and displays altogether the character of purity.

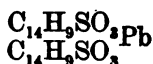
According to its degree of purity, anthracen forms larger or smaller tabular crystals, belonging to the monoclinar system. When perfectly white, they display a beautiful blue fluorescence. As long as they are tinged yellow by chrysogen even in the slightest degree, this phenomenon does not appear. When pure, anthracen is perfectly tasteless and inodorous; it is sparingly soluble in alcohol and ether, moderately soluble in boiling benzol, but less so in the cold. It is similarly soluble in oil of turpentine, and in other hydrocarbons. In ligroin it is less soluble than in benzol. Anthracen melts at  $213^{\circ}$ , distils a little above  $360^{\circ}$ , but sublimes slowly even at  $100^{\circ}$  in small leaflets. With picric acid it forms a compound  $C_{14}H_{10} + 2C_6H_3(NO_2)_3O$ , obtained by dissolving the hydrocarbon in an alcoholic solution of picric acid, saturated at  $30^{\circ}$ – $40^{\circ}$ . It forms fine ruby-red crystals, which are decomposed by water or alcohol, and more readily by alkaline lyes. With a solution of binitroanthraquinon in benzol it forms fine violet tables.

If acted on by chlorine, anthracen is first converted into anthracendichloride,  $C_{14}H_{10}Cl_2$ , which crystallises from ether in yellowish, fusible, and volatile needles, which on treatment with alcoholic potassa become the monochloride,  $C_{14}H_9Cl$ .

The action of bromine produces several products, to be described farther on.

Dry anthracen, treated with nitric acid, or with a mixture of sulphuric and nitric acids, yields oxanthracen or anthraquinon,  $C_{14}H_8O_2$ . At the same time is always formed binitroanthraquinon (Fritzsche's reagent, or oxybinitrophoten).

If treated with concentrated sulphuric acid, there is formed sulphanthracenic acid,  $C_{14}H_9(SHO_3)$ , whose lead salt



crystallises in yellowish white columns.

If heated with hydriodic acid in a sealed glass tube to  $150^{\circ}$ – $160^{\circ}$ , anthracen is first converted into anthracendihydride,  $\text{C}_{14}\text{H}_{10}\text{H}_2$ , but on more prolonged heating there is formed anthracenhexahydride,  $\text{C}_{14}\text{H}_{10}\text{H}_6$ .

If a cold saturated solution of anthracen in benzol is exposed to the rays of the sun, tabular crystals of paraanthracen (paraphoten of Fritzsche) are deposited, very sparingly soluble in benzol, ether, and alcohol. If melted, which takes place not until  $244^{\circ}$ , it is re-converted into anthracen. It is unaffected by ordinary crude nitric acid at the boiling-point, likewise by bromine dissolved in disulphide of carbon. Paraanthracen, therefore, may be distinguished from anthracen by its greater stability, as was observed by Fritzsche.

## HYDRIDES OF ANTHRACEN.

### 1. ANTHRACENDIHYDRIDE, $\text{C}_{14}\text{H}_{10}\text{H}_2$ .

From anthracen it is easy to prepare a hydrocarbon  $\text{C}_{14}\text{H}_{12}$ , which in its behaviour ranks with the aromatic addition-products, and which was named by Graebe and Liebermann anthracendihydride. It is formed both by the reaction of hydriodic acid upon anthracen, and by the reduction of the latter by sodium-amalgam, in an alcoholic solution. The latter procedure is preferable. No hydrogen is added to anthracen dissolved in alcohol, on treatment with zinc-powder and potassa lye, or tin and hydrochloric acid.

#### *Preparation by means of Sodium-amalgam.*

Anthracen dissolved in alcohol is treated with sodium-amalgam till a portion taken out shows the correct melting-point,  $106^{\circ}$  C., or no longer produces a red colour when

heated with picric acid and benzol. With large quantities, it is unnecessary to add as much alcohol as would be required for the solution of the anthracen. It dissolves gradually as it is converted into the dihydride, which is much more soluble in alcohol. Anthracen is heated with about 10 parts of alcohol at 95 per cent. in a flask with an ascending condenser, and pieces of sodium-amalgam are gradually added. It is proper to neutralise the liquid from time to time by the addition of an acid, as the reduction proceeds very slowly in strongly alkaline solutions.

For the complete reduction of the anthracen, heat must be applied for twelve to twenty-four hours, according to the quantity. The bulk of the dihydride is deposited in crystals as the alcoholic liquid cools; that which remains in solution is obtained by distilling off the alcohol, and washing with water. The product thus prepared has its melting-point at  $106^{\circ}$ , and further purification by crystallisation from alcohol is rarely requisite.

*Preparation by means of Hydriodic Acid.*

Anthracen is heated for ten to twelve hours to  $160^{\circ}$ – $170^{\circ}$  in a sealed tube with  $\frac{1}{4}$  part by weight of amorphous phosphorus, and about 5 parts of hydriodic acid boiling at  $127^{\circ}$ . Almost the whole of the phosphorus disappears, and the anthracen is converted into a hydrocarbon, which solidifies on cooling. On opening the tube, some phosphuretted hydrogen escapes, which is generated only in small quantity if the heat is not stronger than is here directed. The hydrocarbon produced is freed from hydriodic acid by washing in water, then dissolved in alcohol, and freed from excess of phosphorus by filtration. It is easily obtained pure by recrystallisation from alcohol, or by distillation.

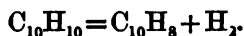
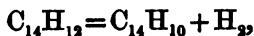
Anthracendihydride crystallises from alcohol in colourless tables, which often resemble naphthalin. The crystals

are small monoclinar tables, with the base  $c=OP$ , bordered by the prism  $p=\infty P$ , and a posterior hemidome  $\alpha=-P\infty$ , which gives the direction of cleavage.

On heating, anthracendihydride melts at  $106^\circ$ , and begins about the same temperature to sublime in colourless shining needles. At  $305^\circ$  it distils without decomposition. It has a peculiar odour, which is rendered more intense by heat. It is insoluble in water, but dissolves freely in alcohol, ether, and benzol. It is easily volatilised along with the vapour of water, and even with that of alcohol. The solid hydrocarbon is not fluorescent, but its solutions display a blue fluorescence. If heated with picric acid in alcohol, there is no red colouration, and no compound corresponding to that of anthracen with picric acid has hitherto been obtained.

The properties of anthracen and of its dihydride differ respectively chiefly as regards fusibility, boiling-point, and solubility.

As already stated, the dihydride is capable of being distilled without decomposition; but if passed through a tube at a low red heat, it is completely resolved into anthracen and hydrogen. Anthracendihydride is also split up at dull redness, exactly like naphthalindihydride, according to Berthelot's statements:



If anthracendihydride is heated to  $100^\circ$  with concentrated sulphuric acid, it is dissolved with the escape of sulphurous acid in abundance. After applying heat for a short time, a hydrocarbon is deposited on the addition of water, and after re-crystallisation from alcohol, it agrees perfectly in its melting-point and its other properties with anthracen. Besides anthracen, the sulphacids of the latter body are formed as secondary products.

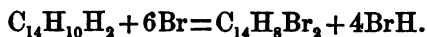
Sulphuric acid acts, therefore, upon anthracendihydride as an oxidising agent, and reconverts it into anthracen :



If to a molecule of anthracendihydride, dissolved in disulphide of carbon, a molecule of bromine is added by drops, hydrobromic acid escapes in abundance, and there remains, after evaporation of the disulphide of carbon, a crystalline mass, which is resolved by alcohol into a substance readily soluble in this liquid, and one almost insoluble. The former is undecomposed anthracendihydride, melting at  $106^\circ$ ; the latter is bibromanthracen, which melts between  $219^\circ$  and  $220^\circ$ . Anthracen is not obtained from this reaction. The action of 2 mol. bromine upon 1 mol. of anthracendihydride is similar, but the yield of bibromanthracen is greater. It is formed most abundantly by the reaction of 3 mol. bromine and 1 mol. anthracendihydride. The bibromanthracen thus obtained agrees in every respect with that obtained directly from anthracen, as described below.

The formation of bibromanthracen will be readily understood from the above experiments, which show that the action of bromine upon anthracen is most complete when 3 mol. of the former act upon 1 mol. of anthracendihydride.

Two atoms of hydrogen are carried away by two atoms of bromine, whilst simultaneously bromine replaces two more atoms of hydrogen.



Anthracendihydride is readily oxidised by chromate of potassa and sulphuric acid, and converted into the characteristic oxidation product of anthracen,—anthraquinon. This agrees in every respect with that to be described below, sublimes in the same yellow needles, and melts at  $275^\circ$ . If anthracendihydride is heated with dilute nitric acid, anthraquinon is obtained along with nitrated products, amongst

which binitroanthraquinon may be recognised by the characteristic compound which it forms with anthracen.

For the oxidation of anthracendihydride we require four atoms of oxygen, which are furnished by the oxidising agent, chromic or nitric acid.



An atom of oxygen effects the removal of the two added atoms of hydrogen, and the three others complete the conversion into anthraquinon, by substituting the group  $(\text{O}_2)''$  for two atoms of hydrogen.

Anthracendihydride in an alcoholic solution cannot be further reduced by sodium-amalgam. Even if the action is prolonged for days, there are formed only traces of a compound richer in hydrogen, whilst the melting-point sinks for some degrees. Hydriodic acid (melting-point  $127^\circ$ ) has no further reducing action upon anthracendihydride at  $160^\circ$ , but at  $200\text{--}220^\circ$ , converts it into anthracenhexahydride.

An alcoholic solution of iodine at the boiling-point has no effect.

If we survey the behaviour of the hydrocarbon just described,  $\text{C}_{14}\text{H}_{12}$ , its complete agreement with the behaviour of the so-called addition-products of the aromatic series cannot be ignored. In all the reactions of anthracendihydride there appears the characteristic phenomenon, that compounds are always formed belonging to the anthracen type, poorer in hydrogen; this agrees with the observations on hydrophthallic acid, hydromellitic and quinic acids, from which there have been hitherto obtained merely substitution-products of benzol, but no substances belonging to a type rich in hydrogen. Graebe and Liebermann, therefore, selected for the first reduction-product of anthracen the name anthracendihydride, which agrees with the name benzol-hexachloride,  $\text{C}_6\text{H}_6\text{Cl}_6$ . The formation of anthracendihydride must, therefore, be regarded as a transformation of the

double combination of the carbon atoms of anthracen into a single one, and saturation of the bonds thus set free, by two atoms of hydrogen. By the reformation of anthracen and its derivatives from the dihydride, occasioned by the action of various reagents, the more intimate combination of the two atoms of carbon by every two unities of affinity is reproduced.

For deciding on the chemical character of anthracen-dihydride, it is interesting to compare it with stilben, which contains the same number of atoms of hydrogen and carbon. According to the researches of Limpricht and Schwanert, stilben has the rational formula :



and behaves in many respects like ethylen. It combines directly with two atoms of bromine, and forms bromide of stilben, corresponding to bromide of ethylen, whilst hydrogen is withdrawn from anthracendihydride by bromine. On oxidation, stilben yields oil of bitter-almonds  $\text{C}_6\text{H}_5\text{C}=\text{O}$ ,  $\text{H}$  and benzoic acid  $\text{C}_6\text{H}_5\text{COH}$ ,  $\text{O}$ , its molecule being split up. Anthracendihydride, on the other hand, is converted into anthraquinon.

*Anthracenhexahydride*,  $\text{C}_{14}\text{H}_{10}\text{H}_6$ .—Anthracenhexahydride is the second reduction-product obtained by the action of hydriodic acid upon anthracen. A tetrahydride does not appear to exist. The substance formerly described by Graebe and Liebermann as a tetrahydride, the analysis of which agreed very well with the formula  $\text{C}_{14}\text{H}_{14}$ , proved on closer examination to be a mixture. It is extremely troublesome to obtain the hexahydride in quantity, as the sealed tubes often explode from the liberation of phosphuretted hydrogen.

The best material for its preparation is anthracendihydride. This is heated for ten or twelve hours in sealed tubes

to 200° to 220°, along with  $\frac{1}{4}$  to  $\frac{1}{3}$  part of amorphous phosphorus, and about 5 parts of hydriodic acid (boiling-point 127°). The tubes must be opened with caution, as much phosphuretted hydrogen is always generated. The hydrocarbon obtained is washed with water to remove the hydriodic acid, dissolved in alcohol, and separated by filtration from the residual phosphorus. The mass obtained on evaporation of the alcohol, is pressed between bibulous paper in order to separate the anthracenhexahydride from small quantities of an accompanying liquid body. It is then submitted to distillation, and the portion boiling at 290° is collected separately. Thus is obtained a hydrocarbon, melting at 63°, whose analysis leads to the formula  $C_{14}H_{16}$ .

In its physical properties anthracenhexahydride agrees very closely with the dihydride. It crystallises from solvents in leaflets, and is readily soluble in alcohol, ether, and benzol.

If conducted through an ignited tube, it is resolved into anthracen and free hydrogen. It resists the action of nitric acid much better than the dihydride.

Anthracenhexahydride is formed from anthracen, by the conversion of the double combination of three couples of carbon atoms into a single one, thus enabling six atoms of hydrogen to be taken up.

*Bromine derivatives of anthracen.*—Anderson was the first chemist who studied the action of bromine upon anthracen, and described two compounds, to which he assigned the formulæ,  $C_{14}H_{10}Br_6$ , and  $C_{14}H_8Br_4$ . The former, which he obtained by the action of an excess of bromine upon anthracen, he considers as an addition-product, six atoms of bromine to one molecule of anthracen. From this he prepared the second compound by the action of an alcoholic solution of potassa, and regarded it as bibromanthracen-dibromide. Berthelot, who observed subsequently that hydrobromic acid is formed when bromine reacts upon anthracen, suggested that both these bromine compounds



probably contained two atoms hydrogen less than Anderson had assumed in his formulæ. The behaviour of the former bromine-compound with alcoholic potassa is in favour of this view. An addition-product with six atoms of bromine must, like benzolhexachloride, become a tri-substitution-product, whilst a compound is formed containing four atoms of bromine. Graebe and Liebermann have, therefore, re-examined the bodies described by Anderson, and have ascertained experimentally, that Anderson's formulæ contain two atoms hydrogen too much. Besides these compounds, the above-mentioned chemists have obtained a bibromanthracen and a tribromanthracen. A monobromanthracen has not yet been produced. From anthracen dissolved in disulphide of carbon, there is formed by the reaction of one molecule on exactly two atoms of bromine, bibromanthracen, a corresponding quantity of anthracen remaining unchanged. By lixiviation with alcohol, the anthracen is removed from the sparingly soluble bromine compound, and may by re-crystallisation be isolated, perfectly free from bromine.

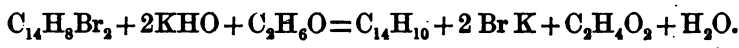
*Bibromanthracen*,  $C_{14}H_8Br_2$ .

As already mentioned, bibromanthracen is formed by the action of bromine upon anthracen, dissolved in disulphide of carbon. It is the only substitution-product formed under these circumstances. Even if more than four atoms of bromine are applied to 1 mol. of anthracen, there is no formation of a compound richer in bromine. For the preparation of bibromanthracen, it is sufficient to diffuse the anthracen in disulphide of carbon, and to add by degrees the calculated amount of bromine. The disulphide of carbon becomes hot, and the bibromanthracen dissolves as it is formed. On cooling it is deposited in fine yellow needles, often above 1 centm. in length, which are purified by recrystallisation from disulphide of carbon, or the homologues of benzol. The portion of bibromanthracen which remains

in solution is obtained by evaporating the disulphide of carbon.

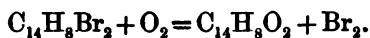
It is very sparingly soluble in alcohol and ether; benzol dissolves it slightly when cold, but more plentifully if heated. It melts at  $221^{\circ}\text{C.}$ , and sublimes undecomposed in long yellow needles.

Neither alcoholic nor aqueous potassa acts at the boiling-point upon bibromanthracen, but the former decomposes it at  $160\text{--}170^{\circ}$  in a sealed tube. Bromide of potassium is separated, and in the tube is found, partly in solution and partly undissolved, a hydrocarbon which is found to be anthracen. In addition to anthracen, Graebe and Liebermann have recognised aldehyd and acetic acid, so that the reaction may possibly be expressed by the following equation :



Chydenius observed an analogous reaction; on causing alcoholic potassa to act upon the bromide of cetylen,  $\text{C}_{16}\text{H}_{30}\text{Br}_2$ , he obtained ceten,  $\text{C}_{16}\text{H}_{32}$ . In both cases the alcohol furnishes the atoms of hydrogen, and is oxidised to acetic acid by the bromine set at liberty.

Anthracen is also obtained from bibromanthracen by heating it in a combustion tube with quick-lime, or soda-lime, the yield being considerable. Bibromanthracen is converted into anthraquinon by oxidising agents, whether by heating with concentrated nitric acid or by adding chromic acid to a solution of bibromanthracen in glacial acetic acid. Heat is applied in either case as long as bromine is evolved, the mixture is diluted with water, the deposited mass is washed with water, dried and sublimed, when anthraquinon is obtained in its characteristic needles. The following equation represents this reaction, the oxygen being obtained from nitric or from chromic acid.

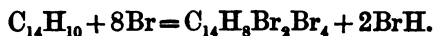


No compound richer in bromine is formed by the action of bromine upon bibromanthracen, dissolved in disulphide of carbon. But in the dry state it readily takes up bromine at common temperatures, and is converted into bibromanthracentetrabromide.

Chlorine has no action under similar circumstances.

*Bibromanthracentetrabromide,  $C_{14}H_8Br_4$ .*

This compound was first obtained by Anderson, who described it as hexabromanthracen. That the formula  $C_{14}H_{10}Br_6$ , given by this chemist, contains two atoms of hydrogen too much, follows from its direct formation from bibromanthracen. According to the method given by Anderson (the action of bromine at ordinary temperatures, and in the state of vapour upon thin layers of anthracen), the preparation succeeds badly, and the yield is small; brown, smeary masses being produced. The reaction succeeds best when the anthracen is in a very fine state of division. Each time hydrobromic acid is evolved in great quantity, which led Berthelot to the view that the bromine was not merely added to the anthracen, but acted also in the way of substitution. The quantity of the bromine used in successful operations points in the same direction. Not six, but eight atoms are required, until the fumes of bromine no longer disappear, which indicates the completion of the reaction. The action of bromine upon dry anthracen is represented, therefore, by the equation :



Bibromanthracentetrabromide may be prepared with greater certainty and convenience from bibromanthracen.

It is spread upon a plate of glass and placed under a glass bell along with the requisite quantity of bromine (4 atoms to 1 mol. of bibromanthracen), contained in a capsule.

The bromine is rapidly absorbed, and according to the quantity employed disappears in a few hours, or in the course of a day, without the evolution of hydrobromic acid. The original yellow compound, when bromine is no longer present, is almost colourless, and is only contaminated with very small quantities of foreign substances. These are removed by washing with cold ether, and on recrystallisation from benzol the bibromanthracentetrabromide is obtained in full purity.

It crystallises in hard, thick, colourless tables; it is insoluble in water; dissolves sparingly in ether, alcohol, and cold benzol, but more plentifully in the latter when boiling. It melts and is decomposed between 170° and 180°. Vapours of bromine and hydrobromic acid escape, and the residual mass consists of pure tribromanthracen, which is formed according to the following equation:



On treatment with alcoholic potassa, 2 mol. of hydrobromic acid are removed and there remains Anderson's tetrabromanthracen:

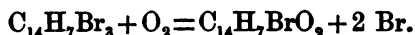


*Tribromanthracen, C<sub>14</sub>H<sub>7</sub>Br<sub>3</sub>.*

This compound is formed by heating the foregoing to 200°, until vapours of bromine and hydrobromic acid no longer escape. The product is purified by recrystallisation from benzol.

It crystallises, like bibromanthracen, in yellow needles, dissolves sparingly in alcohol, but readily in benzol, by which it is distinguished from bi- and tetrabromanthracen. It melts at 160° and sublimes in needles. In tribromanthracen, as in bibromanthracen, two atoms of bromine may be replaced by two atoms of oxygen, by means of oxi-

dising agents. On heating with strong nitric acid (1·4 sp. gr.), or better, with glacial acetic acid and chromic acid, we obtain bromanthraquinon, as described below :

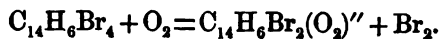


In the same circumstances under which bibromanthracen is converted into bibromanthracentetrabromide, tribromanthracen takes up four atoms of bromine, but the resulting compound has not been closely examined.

*Tetrabromanthracen, C<sub>14</sub>H<sub>6</sub>Br<sub>4</sub>.*

For the preparation of this compound bibromanthracen-bromide is covered with alcohol, heated in the water-bath, and a concentrated aqueous solution of  $\frac{1}{4}$  to  $\frac{1}{3}$  part of hydrate of potassa is added. The colourless mass is immediately converted into yellow tetrabromanthracen, with a great increase of volume. In its properties it agrees with Anderson's tetrabromanthracen, except that he states its melting-point as 238°, whilst Graebe and Liebermann make it 254°. It is very sparingly soluble in water and ether. Benzol dissolves it more plentifully, but is not a good solvent. The hydrocarbons with high boiling-points, such as xylol and also disulphide of carbon, are the best solvents for its recrystallisation.

As in bi- and tribromanthracen, two atoms of bromine in this compound are readily replaced by oxygen. Tetrabromanthracen, dissolved in glacial acetic acid and heated with chromic acid, yields bibromanthraquinon. Nitric acid of different degrees of concentration acts in the same manner. The oxidation succeeds very well with nitric acid of sp. gr. 1·4 and chromate of potassa. The following equation represents the action of oxidising agents upon tetrabromanthracen :

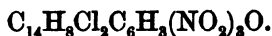


*Bichloranthracen*,  $C_{14}H_8Cl_2$ .

This compound is formed both on the action of chlorine upon anthracen at  $100^\circ$ , and on the prolonged exposure of anthracen to an atmosphere of chlorine at ordinary temperatures. Laurent prepared in the latter manner his bichloranthracen, which is identical with that of Graebe and Liebermann. Laurent's analysis of bichloranthracen agrees very well with the formula  $C_{14}H_8Cl_2$ , if his results are recalculated in accordance with the correct atomic weight of carbon.

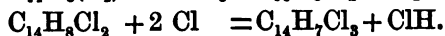
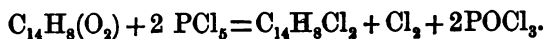
It crystallises in long shining needles which melt at  $209^\circ$ ; it is readily soluble in benzol, sparingly in alcohol, and slightly in ether. The solutions, especially the alcoholic, possess a splendid blue fluorescence. It sublimes in small yellow needles. Bichloranthracen is not attacked by alcoholic potassa at the boiling-point, whereby it is distinguished from anthracenbichloride, a compound obtained by Anderson by the brief action of a very slow current of chlorine, and which is converted by potassa into monochloranthracen,  $C_{14}H_9Cl$ .

Oxidising agents convert bichloranthracen, like the corresponding bromine compound, into anthraquinon. It combines with picric acid, forming a red crystalline compound, whose composition may be represented by the formula—

*Trichloranthracen*,  $C_{14}H_7Cl_3$ .

This compound is obtained by the action of phosphoric pentachloride upon anthraquinon. This reaction completely agrees with those observed in trichlorquinon and bichlor-naphthaquinon, and is a further proof that bioxyanthracen really belongs to the quinones. The formation of trichloranthracen corresponds to both the following equations, since the two atoms of oxygen are exchanged for atoms of chlorine,

and the chlorine set at liberty acts further in the way of substitution—



This reaction, however, is not so well defined as in the quinones of benzol and naphthalin, since a part of the phosphoric chloride gives off chlorine, which acts substitutionally, whence more highly chlorinised products accompany the trichloranthracen.

In the preparation of this compound the following procedure may be adopted. Anthraquinon is heated for several hours to 190°–200° in a sealed tube along with two molecules of phosphoric pentachloride, with an addition of phosphoroxychloride. On opening the tube a strong pressure is observed, and hydrochloric acid escapes in abundance. The contents of the tube are treated with water, and the portion insoluble in water is recrystallised from alcohol. Trichloranthracen is thus obtained in yellow needles, which may be sublimed without decomposition, and are not affected either by alcoholic or aqueous potassa. They dissolve with difficulty in alcohol and ether, but readily in benzol.

*Tetrachloranthracen, C<sub>14</sub>H<sub>6</sub>Cl<sub>4</sub>.*

If a stream of chlorine is passed over anthracen at 170°–180° there is a copious escape of hydrochloric acid, and the mass melts. The product obtained, which congeals on cooling and is probably bibromanthracen chloride (?), is not easily purified. Graebe and Liebermann therefore treated it at once with alcoholic potassa, and recrystallised it from benzol. The analysis leads to the formula C<sub>14</sub>H<sub>6</sub>Cl<sub>4</sub>.

From benzol tetrachloranthracen crystallises in gold-yellow needles arranged in stellar groups; it is slightly soluble in alcohol, somewhat more freely in benzol when hot, but scarcely when cold. Its melting-point is about 220° C.

Nitric acid converts tetrachloranthracen into bichloranthraquinon.

*Disulphodichloranthracenic acid*,  $C_{14}H_8Cl_2 \cdot 2SO_3$ .

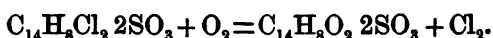
*Monosulphodichloranthracenic acid*,  $C_{14}H_8Cl \cdot SO_3$ .

Dichloranthracen dissolves gradually in fuming sulphuric acid, and the green solution thus formed becomes yellow on dilution with water. The product thus obtained contains disulphodichloranthracenic acid, and probably also monosulphodichloranthracenic acid, but Perkin's proof of the presence of the latter is not quite complete.

Disulphodichloranthracenic acid has a yellow or orange colour, and dissolves readily in water; the dilute solution is highly fluorescent. The acid is bibasic, forming salts of the formula  $C_{14}H_6M_2Cl_2 \cdot 2SO_3$ ; several of which are sparingly soluble in water and of a yellow or orange colour.

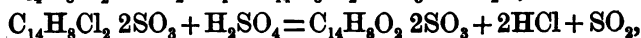
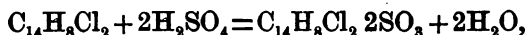
Dibromanthracen dissolves likewise in fuming sulphuric acid with a green colour, and yields compounds analogous in behaviour and constitution to those formed by dichloranthracen under similar circumstances.

If the chloro- or bromosulpho-acids are exposed to oxidising agents, they exchange chlorine or bromine for oxygen, and are converted into anthraquinodisulphuric acid :

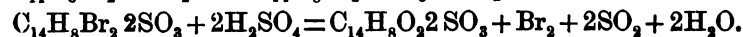
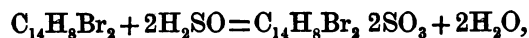


The termination of the reaction is easily recognised by the disappearing of the fluorescence.

If dichlor- or dibromanthracen is treated with concentrated or fuming sulphuric acid, and if the temperature is gradually raised, the sulpho-acids are formed at first and pass afterwards into anthraquinodisulphuric acid, the process being represented by the following equations :



or in cases of dibromanthracen—





*Anthracencarbonic acid, C<sub>14</sub>H<sub>9</sub>CO<sub>2</sub>H.*

Whilst neither Berthelot nor any other chemist has succeeded in repeating Harnitzky's synthesis of benzylchloride from benzol and chlorocarbonic acid, and whilst naphthalin shows itself equally indifferent towards this compound, Graebe and Liebermann succeeded in preparing anthracencarbonic acid from anthracen with the aid of this body.

On heating anthracen with chlorocarbonic oxide to 100° in sealed tubes, both bodies remain unaffected. But when the temperature rises to about 180° the contents of the tube take a different appearance, and abundance of hydrochloric acid is evolved on opening the tube. It is therefore most convenient to heat the tubes for ten or twelve hours to 180°–200° C. To raise the temperature higher is not to be recommended, since the yield is then smaller and more by-products appear. Whether, according to Berthelot's statement, the formation of the acid chloride ceases at 230° is not yet decided.

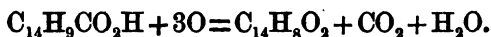
After the action of the chlorocarbonic oxide upon anthracen is at an end, the tubes are placed in a freezing mixture and then opened, whereon streams of carbonic acid escape, whilst the unconsumed chlorocarbonic oxide is left behind. To recover the latter the tube is connected with a glass U-tube, which is plunged into a freezing mixture; the other tube is placed in warm water, so that the chlorocarbonic oxide distils over and is recondensed in the cold U-tube. The contents of the tube, consisting of yellow crystals and a brown resinous mass, are digested with soda-lye, which leaves the brown substances undissolved, whilst yellow flocks are deposited on adding an acid to the filtrate. By recrystallisation from boiling water, which is only practicable on a small scale on account of the slight solubility, or better from alcohol, anthracencarbonic acid is obtained in fine needles.

Anthracencarbonic acid forms yellowish acicular crystals. Graebe and Liebermann believe, however, that the yellow colour is merely due to an impurity which adheres very tenaciously to the acid. It dissolves very readily in ether, alcohol, and glacial acetic acid, very sparingly in water, but more plentifully in hot than in cold. It melts at  $206^{\circ}$ , but is slowly decomposed into anthracen and carbonic acid. Whilst determining the melting-point we observe a continual rise of gas bubbles out of the floating mass. This decomposition begins at lower temperatures; leaflets of anthracen begin to appear at  $150^{\circ}$  if the compound is heated in a test-tube in the oil-bath.

Anthracencarbonic acid is also decomposed if heated with soda lime. If the experiment is conducted in a combustion tube, leaflets are deposited in the cold anterior portion, which melt at  $213^{\circ}$  C. and give the characteristic reaction with picric acid.

Its behaviour with oxidising agents is very peculiar. If it is dissolved in glacial acetic acid, mixed with chromic acid, and heated, carbonic acid escapes, and on cooling long yellow needles of anthraquinon are deposited. Dilute nitric acid with the aid of heat likewise converts anthracencarbonic acid into anthraquinon, which, however, is contaminated with nitro compounds.

The oxidation is represented by the equation—



In contact with bases and carbonates, anthracencarbonic acid behaves like a powerful organic acid, and forms the corresponding salts.

The silver salt,  $\text{C}_{14}\text{H}_9\text{CO}_2\text{Ag}$ , is obtained by heating an alcoholic solution of the acid with recently precipitated carbonate of silver, driving off the alcohol and dissolving in water. On concentration the salt, which is easily soluble in

water, is deposited as a yellowish crystalline powder. Under the microscope it exhibits a columnar structure.

The barium salt,  $(C_{14}H_9CO_2)_2Ba$ , is prepared from carbonate of baryta and the free acid. It is readily soluble in water, but scarcely more so at the boiling-point than at common temperatures. On evaporating the solution, yellowish indistinctly developed crystals are deposited, which do not lose weight if heated to  $170^{\circ}$ – $180^{\circ}$  C.

C. Liebermann and G. von Rath have discovered an isomer of anthracencarbonic acid, by treating anthracenomonosulphuric acid with dehydrated prussiate of potash and subsequently with alcoholic potassa. The acid thus obtained has a great resemblance to the one above described, but still differs from it essentially in many points. It is prepared by digesting anthracen at the lowest possible temperature—in order to obtain the largest amount of sulphacid—with sulphuric acid; the compound acids obtained are converted into potassic salts, and without any further separation are mixed with an equal weight of perfectly dehydrated yellow prussiate, and distilled in small portions in small glass retorts, which must be almost entirely filled with the mixture. This process gives the best, though still very trifling, yield of an orange distillate, which solidifies on cooling, and which still contains anthracen along with the nitril. As the two compounds are not easily separated, the mass is boiled at once for several days with alcoholic potassa till the development of ammonia ceases. The liquid, freed from alcohol and filtered on the addition of hydrochloric acid, deposits an acid in yellow flakes. The yield is at most 5 per cent. of the anthracen employed, evidently because a part of the material is decomposed at the temperature of the treatment with prussiate of potash.

For complete purification, the compound is converted into a readily soluble barytic salt by digestion with carbonate of baryta; a small quantity of a sparingly-soluble barytic salt,

perhaps belonging to the dicarbonic acid, remains behind. The re-precipitated acid is again treated in the same manner, and then crystallised from alcohol.

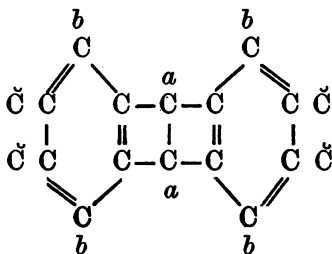
Anthracencarbonic acid is insoluble in water, sparingly soluble in benzol, more readily in alcohol, ether, and glacial acetic acid. From alcoholic solutions, saturated when hot, it is deposited on cooling in fine yellow needles; if the concentration is more rapid, it appears almost amorphous. The acid decomposes carbonates, and forms chiefly soluble salts. The barium and calcium salts dry up to amorphous, pale yellow masses, which become anhydrous at  $130^{\circ}\text{C.}$ , and have then the composition  $(\text{C}_{14}\text{H}_9\text{CO}_2)_2\text{Ba}$ , and  $(\text{C}_{14}\text{H}_9\text{CO}_2)_2\text{Ca}$ . The sparingly-soluble lead salt is thrown down in flakes on mixing the solution of the ammonia-salt with a solution of acetate of lead. The barium-salt is not decomposed by carbonic acid, but the ammonium-salt loses its base on evaporation. The solutions of the acid and its salts fluoresce from greenish to blue, according to their degree of purity. The acid is always precipitated of a yellow colour, even from solutions free from the slightest yellow tint.

If anthracencarbonic acid is heated with soda-lime, or if its lime or baryta-salt is heated alone, anthracen is obtained.

So far this acid and its salts possess an external resemblance to the anthracencarbonic acid described by Graebe and Liebermann, and obtained by another process. A slight distinction appears on crystallising the acid from alcohol, since the earlier-described acid, on the evaporation of the solvent, is deposited in long needles.

Considering our slight acquaintance with the monosubstitution-products of anthracen, it seems important to decide whether the two anthracarbonic acids are identical or isomeric, since in the latter case we may infer the possibility of isomeric monosubstitution-products in general.

The constitution of anthracen at present assumed—

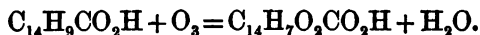


would admit of three series of isomeric monosubstitution products (in *a*, *b*, and *c*). The experiments of Liebermann and V. Rath have proved the isomerism of this acid with that of Graebe and Liebermann.

The essential distinctions are as follows :

The acid of Graebe and Liebermann melts at 206° C., but passes partially even at 150° C. into anthracen, with evolution of carbonic acid. The new acid does not soften until 220°–230° C., and melts irregularly at 260°; but even if the temperature is maintained for some time at 280° C., there is no strong evolution of gas perceptible. At higher temperatures the acid sublimes, entirely without decomposition, in beautiful orange-yellow needles, which exhibit the same peculiarity in melting, dissolve in dilute ammonia, from which they are re-precipitated by acids.

If oxidised with chromic and glacial acetic acids, the acid of Graebe and Liebermann yields anthraquinon; but the new acid produces mere traces of this substance, and forms principally anthraquinoncarbonic acid. An excess of oxidising agents, however, strongly attacks the anthraquinoncarbonic acid, and reduces the yield. The oxidation of anthracencarbonic acid takes place according to the equation—



The above properties of the two isomeric anthracencarbonic acids are most readily explained, if we assume that the

acid formed by means of chlorocarbonic oxide has its carboxyl group at *a*, whilst that obtained from anthracensulphuric acid has the same group at *b* or *c*. If an acid of the former constitution is oxidised, carbonic acid must be evolved, because the oxygen of the quinon passes to the carbon atoms *a*: in the latter the oxidation of the carbon atoms at *a* can be completed without displacing the groups at *b* or *c*.

*Methylantracen*,  $C_{15}H_{12}$ .

This compound was obtained by Weiler and Fischer on passing dimethylphenylmethan or dimethylphenylethan through ignited tubes filled with fragments of pumice-stone. The reaction takes place according to the following equation—



In order to maintain and purify the methylantracen, the coloured and adhesive matter found in the receiver is first washed with a little ether and alcohol, in order to purify it from any undecomposed residue of ditolylmethan, and then either recrystallised from glacial acetic acid and alcohol, or by preference converted into finely crystalline picric acid compound, which in turn is decomposed with ammonia.

Its melting-point varies from  $198^{\circ}$ – $201^{\circ}$  C., according to the method of purification employed.

Methylantracen is insoluble in water, sparingly soluble in ether, alcohol, glacial acetic acid, and is deposited from solutions saturated at high temperatures in beautiful white shining scales, tinted with a slight yellowish shade. It dissolves readily in bisulphide of carbon, chloroform, and benzol, but very sparingly in methylic alcohol, acetone, and petroleum. It is precipitated from its solutions on the addition of water in white flocks, which, when dry, become gradually yellow on prolonged exposure to the air. Concentrated or fuming

nitric acid dissolves methylantracen slowly in the cold, but more rapidly at a moderate heat. The action of concentrated or fuming sulphuric acid is similar.

Bromine, dissolved in disulphide of carbon, has a very violent action upon this hydrocarbon, dissolved in the same medium; torrents of hydrobromic acid escape, whilst finely crystalline yellow bromine compounds are formed.

With picric acid it yields a compound crystallising in fine, long, dark red needles, which very closely resemble anthracen-picric acid, and are decomposed by water or alcohol, but more readily by aqueous alkalis and ammonia.

Methylantracen sublimes in large beautiful scales, which, when perfectly white, display a fine blue fluorescence.

If methylantracen is oxidised with glacial acetic acid and chromic acid, we obtain not methylantraquinon, but anthraquinon-carbonic acid, melting at  $283^{\circ}$ , which yields anthraquinon on heating with soda-lime. If methyl-antracen is dissolved in excess of alcohol, and if ordinary concentrated nitric acid is afterwards added, a brisk reaction is set up, owing to the oxidation of the alcohol. The alcohol is allowed to evaporate spontaneously down to about one-third, and a little water is then added. On cooling, a yellow crystalline matter is deposited, which is well washed with water. The filtered solution is mixed with water, in order to obtain the residue of the dissolved body. This substance is methylantraquinon, and is best purified by sublimation, when it takes the form of thin ramified needles or leaflets.

*Dibrommethylantracen,  $C_{10}H_8Br_2$ .*

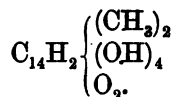
If methylantracen in disulphide of carbon is treated with two molecules of bromine, there escape torrents of hydrobromic acid; and we obtain, when the reaction is completed, and the disulphide of carbon is expelled, a bromine compound, which crystallises from chloroform, glacial acetic acid, &c.,

in fine golden yellow needles, which sublime in large thin needles, and melt at  $156^{\circ}$ .

*Dimethylantracen*,  $C_{16}H_{14}$ .

This compound was first obtained by Van Dorp, who was led to it during the examination of a tinctorial substance prepared from cochineal. If carmine dissolved in sulphuric acid is heated at  $120^{\circ} C.$ , the yellowish-red colour of the liquid becomes violet, whilst  $CO_2$  and  $SO_2$  are evolved. After the temperature has been maintained for a time at  $140^{\circ}$ – $150^{\circ}$ , the solution is poured into water, and the new colour is obtained as a brown flocculent precipitate. After being washed and dried, it is extracted with boiling alcohol, and the alcoholic solution is evaporated. This compound, which was named ruficoccin by Liebermann and Van Dorp, is sparingly soluble in cold water, a characteristic by which it is distinguished from carmine and from carminic acid. It dissolves in alcohol with a beautiful yellow fluorescence, sublimes partially in red vapours, which condense in yellowish-red needles, and with mordants dyes shades resembling those of cochineal, although less brilliant. Its analysis leads to the formula  $C_{16}H_{12}O_6$ .

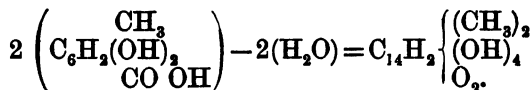
From the origin and behaviour of ruficoccin, which approximate very closely to those of rufigallic acid and the colouring matter of opianic acid,  $C_{14}H_8O_6$  (deducible from anthracen), Liebermann and Van Dorp concluded that it must contain the complex of dimethylantracen, and have the constitution



Its origin is readily intelligible, if we assume that the substance which on nitration induces the formation of nitro-



coccusic acid is joined to the molecule from which water is removed.

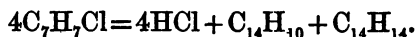


This view is strongly supported by the behaviour of ruficoccin with ignited zinc-dust. The result is a hydrocarbon resembling anthracen, melting at a high temperature, subliming in white leaflets, and forming a red compound with picric acid. After repeated re-crystallisation, this substance melts at  $190^\circ$ , which is below the melting-point of anthracen.

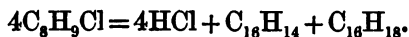
Liebermann and Van Dorp at first considered this substance as dimethylantracen; but subsequent researches rendered it probable that it contains two atoms less hydrogen.

Van Dorp next attempted to arrive at dimethylantracen in another manner, in order to compare it with the hydrocarbon obtained from cochineal.

By heating benzylchloride and water in sealed tubes, Limpricht obtained anthracen according to the equation—



If the reaction with xylylchloride,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_3 \\ \text{Cl} \end{array} \text{CH}_3$ , is analogous, the result must be dimethylantracen.

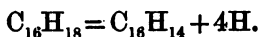


The difficulty of preparing large quantities of xylol induced Van Dorp to make the experiment with coal-tar xylol, which yields chiefly isophthalic acid, and only a small proportion of the terephthalic acid.

By acting with chlorine upon boiling xylol, we obtain after repeated fractionation a product boiling between  $190^\circ$  and  $200^\circ$ , which consists chiefly of the desired xylyl chloride.

If this is heated along with water in sealed tubes to 210° C., we obtain a brown oil of an aromatic odour, very little of which, on fractionation, passes over below 230°. The thermometer then rises gradually up to the boiling-point of mercury, whilst a light yellow oil distils over. Subsequently a crystalline body condenses in the neck of the retort, and finally semi-solid products appear. To obtain the crystalline body in a state of purity is not easy, as the above-mentioned admixtures adhere to it very obstinately. The substance can only be obtained in quantity by taking a considerable amount of the chloride, and submitting it to repeated distillation, decantation, and recrystallisation from glacial acetic acid. After repeated purifications, its ultimate analysis yielded the numbers required for dimethylantracen.

The above-mentioned oil, obtained on the distillation of the product of the reaction of xylchloride with water, if distilled through ignited tubes, which are best filled with pumice or lime, is completely converted into dimethylantracen. This is then collected in the cold anterior portion of the tube, and is purified by distillation. This transformation of the oil seems to occur partially during ordinary distillation, since it deposits crystals; it is, therefore, difficult to purify it so far, that it may be regarded with certainty as a homogeneous body, and analysed as such. From its elevated boiling-point it appears to be a product of the condensation of several molecules of xylol, and that it is formed from xylol in the same manner as the compound  $C_{14}H_{14}$  in Limpricht's synthesis of anthracen. The analogous compound  $C_{16}H_{18}$  might be transformed into dimethylantracen by the abscission of H.



This view is supported by the fact that the liberation of H is observed on passing the oil through ignited tubes.

Dimethylantracen has a strong outward resemblance to anthracen ; it is readily obtained in large shining leaflets, to which a faint yellow colour obstinately adheres.

If cautiously sublimed it becomes pure white, with the blue-violet fluorescence which also characterises pure anthracen. Its melting-point is about  $200^{\circ}\text{C}$ . It dissolves in the usual solvents in about the same proportions as anthracen. A characteristic picric compound has not been obtained.

If dissolved in glacial acetic acid, it is readily oxidised, by the addition of chromic acid, to a substance readily soluble in glacial acetic acid, insoluble in potassa, melting at  $153^{\circ}$ , and subliming in yellow needles. The numbers obtained on analysis agree tolerably with the formula of dimethylantraquinon. There is found, at the same time, a small quantity of a second substance insoluble in potassa, sparingly soluble in glacial acetic acid, which sublimes in yellow needles, and has a higher melting-point.

It was not found practicable to obtain a colouring matter corresponding to alizarin by converting this oxidation-product into a sulpho-acid and subsequent fusion with potassa. The mass took a transient violet colour, but the colouring matter was immediately decomposed.

In spite of all these observations, Zincke doubts the formation of dimethylantracen, especially as Van Dorp did not succeed in transforming dimethylantracen as a body of its composition requires.

*Anthraquinon*,  $\text{C}_{14}\text{H}_8\text{O}_2$ .

As was already mentioned in treating of anthracen, the oxidation-product first obtained by Laurent and named by him, firstly paranaphthalose, and afterwards anthracenuse, is identical with Anderson's oxanthracen. Graebe and Liebermann adopted none of these names, but called it anthraquinon because it is derived from anthracen in the same

manner as quinon from benzol, and as its properties can thus best be explained. That the two atoms of oxygen are connected together in the quinon manner, may be inferred from the circumstance that they replace two univalent atoms of hydrogen in anthracen, and can be again replaced by hydrogen. This substitution, however, is only possible when the oxygen atoms have the same value as the hydrogen atoms; whence it follows that one valence of the oxygen is satisfied by mutual combination.

That the two atoms of oxygen, further, are combined with the two middle atoms of carbon closing the two benzol rings, is proved by the formation of anthraquinon and of its derivatives from phthalic acid and benzoic acid; further, inversely, the formation of phthalic acid from anthracen and its derivatives. The synthesis of anthraquinon from phthalic acid further proves the ortho-position of the two CO groups in at least one of the benzol rings; the corresponding position in the second benzol ring is very probable, on the one hand, on account of the ready oxidation of the anthraquinon derivatives,—a fact which in itself points to an ortho-derivation; and, on the other hand, on account of the formation of quinizarin from phthalic acid and hydroquinon. If we take hydroquinon for a para-derivative, there remain for the two atoms of carbon, supposing that one hydroxyl is adjacent to one carbon, only the positions 1·2, and 1·4; but the properties of the anthraquinon derivatives favour the position 1·2, rather than 1·4.

Among the derivatives of anthraquinon, the position of the substituents is known only in alizarin, and those derivatives from which alizarin is formed, as alsoquinizarin. In alizarin, as in pyrocatechin, the two hydroxyls are in the ortho-position; but in quinizarin, as in hydroquinon, in the para-position. If it were possible to produce an anthraquinon derivative from resorcin, the positions of the two carbon atoms 1·2 would be proved. Whether in anthraflavic acid,

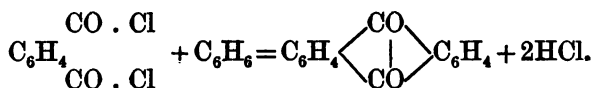
isoanthraflavic acid, and chrysophanic acid, the hydroxyls are contained in one and the same benzol-ring or distributed in both, has hitherto not been demonstrated; but the latter view seems very probable, and could be demonstrated if oxyphthalic acid could be obtained, or if iso- and terephthalic acid yielded compounds like those formed by phthalic acid with phenol.

The formation of anthraquinon from benzoic acid further allows anthraquinon to be regarded as a double keton, inasmuch as on the distillation of benzoate of lime the two residues of benzoic acid combine, and caustic lime is produced. Here also the two oxygen atoms combine with each other in the manner of quinon.

Among the numerous synthetic methods for the formation of anthraquinon derivatives, the synthesis of Baeyer and Caro takes a prominent place. It generalises the method first discovered by Baeyer and Grimm, the products of which—quinizarin, formed from phthalic acid, and hydroquinon—were previously unconnected. By this means it has become possible to enter more profoundly than heretofore into the nature of anthraquinon.

Phthalic acid acts upon the phenols in a twofold relation. It either combines with one or two molecules of phenol. In the former case there is produced an anthraquinon-derivative, and in the second a phthalein. These two reactions were first only observed in case of hydroquinon; whilst in case of the remaining phenols only the phthaleins were known. Subsequently the formation of anthraquinon was established in the case of phenol and pyrocatechin. The conditions for this reaction are elevated temperatures either with or without dehydrating agents. These agencies, when moderately applied, produce phthaleins, but if intensified, they give rise to anthraquinons. The phenols are divided according to their behaviour into two classes. Resorcin and pyrogallie acid yield phthaleins even without

the application of sulphuric acid, but no anthraquinons can be obtained from them. Phenol, hydroquinon, and pyrocatechin do not act upon phthalic acid without the addition of sulphuric acid, but then there are formed both phthaleins and anthraquinons. By this synthetic method there have been obtained oxyanthraquinon, erythroxyanthraquinon, alizarin, and quinizarin. But even before this synthesis of Baeyer's and Caro's was known, Piccard obtained anthraquinon from phthalic acid, and he was led to this synthesis by the observation of Weith and Bindschädler, that on sulphating anthraquinon phthalic acid was formed. He selected Finke's method, the separation of hydrochloric acid from a chloride and a hydrocarbon—in this case phthalic chloride and benzol—according to the following equation :

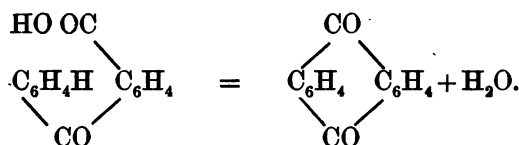


The result confirmed his expectation. Pure anhydrous phthalic acid was converted by means of phosphoric chloride into phthalic chloride, and the latter, after rectification at 270°, was heated for twelve hours in a sealed tube to 220°, along with benzol and zinc powder. After extraction at a boiling heat with alcohol and soda-lye, when a not inconsiderable amount of a brown matter passed into solution, the residue, on sublimation, yielded the well-known yellow needles of anthraquinon. The yield was small, so that it is doubtful whether the above formula expresses the main reaction. Piccard, however, proved beyond doubt that the body obtained was really anthraquinon, by an analysis according to Luck, and by conversion into alizarin.

After Behr and Van Dorp had shown that  $\beta$ -benzyltoluol, as also that  $\beta$ -tolylphenylketon, can be respectively transformed into anthracen and anthraquinon, whilst this transformation is not successful with the corresponding member

of the para-series, they investigated the two benzoylbenzoic acids in the same respect, and found that their behaviour corresponded with that observed in benzyltoluol.

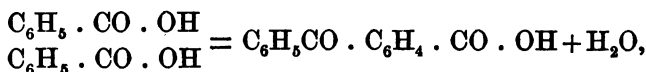
Anthraquinon is formed from  $\beta$ -benzoylbenzoic acid, by the removal of water :



Behr and Van Dorp employed anhydrous phosphoric acid as a dehydrating agent. Two parts  $\text{P}_2\text{O}_5$ , and one part of  $\beta$ -benzoylbenzoic acid were mixed, sand was added and the mass distilled ; the distillate was pure anthraquinon.

Better results were obtained when the above-mentioned mixture was heated for some hours to  $200^\circ$  in the oil-bath, and the anthraquinon formed extracted by means of benzol.

Parabenzoylbenzoic acid, if treated in the same manner, yields no anthraquinon. Small quantities of anthraquinon were also obtained on distilling benzoic acid with  $\text{P}_2\text{O}_5$  ;  $\beta$ -benzoylbenzoic acid having been evidently formed from two molecules of benzoic acid with loss of water :

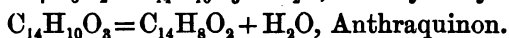
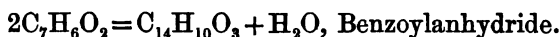


which then again loses a molecule of water, and is condensed to anthraquinon.

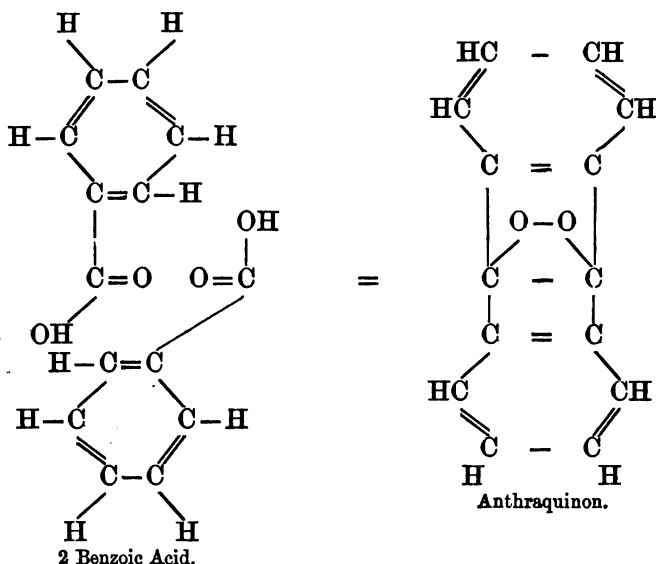
The formation of anthraquinon on the distillation of the benzoate of lime, which was also observed by Kékulé and Franchimont, depends in any case upon an analogous process, save that in one case  $\text{H}_2\text{O}$  is split off, and in the other  $\text{CaH}_2\text{O}_2$ . Anthraquinon is also probably formed during the distillation of  $\beta$ -benzoylbenzoate of lime.

The formation of anthraquinon from benzoate of lime may

appear also as a second anhydride of benzoic acid. We have, namely :



This condensation could be readily explained by the following formula :



As already stated, Kékulé and Franchimont obtained anthraquinon as a secondary product from the preparation of benzophenon. Benzophenon was obtained by the distillation of benzoate of lime, without the addition of quick-lime. When the benzophenon, already partially purified by distillation, was recrystallised from ether, there appeared upon the voluminous crystals of benzophenon fine yellow needles, relatively sparingly soluble in ether. The portion of the benzophenon boiling at a higher temperature yielded a larger quantity of this substance. The same needles were also deposited on the addition of ether to the portion which



distilled over at about  $340^{\circ}\text{C}.$ , and no longer solidified. After repeated recrystallisation from hot benzol, these crystals displayed the exact composition and the properties of anthraquinon. They melted at  $275^{\circ}$ , sublimed below their melting-point, showed the characteristic red colour when heated with zinc-powder and potassa-lye, and when heated with zinc-powder alone produced anthracen.

For the industrial preparation of anthraquinon, anthracen is employed, which, after a more or less perfect purification, is treated with oxidising agents, such as chromic acid, nitric acid, &c.

In order to prepare anthraquinon with nitric acid, it is boiled with acid of 1.2 sp. gr., the yellow mass which separates out is well washed and sublimed. In this procedure, employed by Laurent and Anderson, nitro-products are always formed along with anthraquinon, which impede the purification, and if the method is used on the large scale, are lost on the ultimate conversion into alizarin. It is better, therefore, to employ chromic acid or a chromate.

For the preparation of small quantities the best agents are glacial acetic acid and chromic acid. Anthracen is dissolved in hot glacial acetic acid, and chromic acid, dissolved in the same manner, is added as long as reduction takes place. Needles of anthraquinon are deposited, and that which remains in solution is thrown down on the addition of water. The resulting mass is best purified by distillation or sublimation, when the anthraquinon is obtained pure. Instead of chromic acid, chromate of potash may be used, either alone or with sulphuric acid. The anthracen is dissolved as before in hot glacial acetic acid, and two parts of powdered chromate of potash are added. The reduction of chromic acid begins forthwith, heat being evolved. As the reaction slackens, it is aided by the heat of the water-bath, till the solution takes a deep green. It is then diluted with water, and the mass which separates out is well washed,

dried, and distilled. Anthraquinon distils over, whilst a considerable quantity of chromiferous charcoal remains behind. The bye-products which form this charcoal are more abundant when chromate of potash is used than in case of chromic acid. Perhaps they agree with the chromated products formed from phenol and cresol on oxidation with chromate of potash and glacial acetic acid. Like these, they leave, after being heated, a pyrophoric mixture of carbon and chromic oxide. Since also carbazol on oxidation with chromic acid yields a chromiferous oxidation-product, the chromiferous charcoal may have this origin when the anthracen employed contains carbazol.

In the preparation of anthraquinon on the large scale chromic acid is used, or at least a mixture of chromate of potash and sulphuric acid. The anthracen, preferably sublimed, is diffused in water, the corresponding amount of bichromate of potash is added, the mixture boiled, and the calculated quantity of sulphuric acid is run in. After the completion of the reaction, the liquid is allowed to cool, filtered, the product is well washed with water and dried.

The chrome solutions are either allowed to crystallise, when the crystals of chrome-alum may be applied to dyeing purposes, or they may be reconverted into chromate of potash.

The dried crude anthraquinon is heated with sulphuric acid to about  $120^{\circ}$  C.; the black liquid mass is diluted with water, filtered, washed well and dried. The anthraquinon is thus obtained as a greyish-green impalpable powder, containing 93 to 96 per cent. of pure anthraquinon.

Another process, which, if it could be carried out on the large scale, would be certainly the least expensive and most practical, has been patented in England by F. Baeyer, F. Weskott, and A. Siller. According to this process, one part of anthracen is heated with one to five parts of manganese to about  $200^{\circ}$ , when the anthraquinon is obtained direct as a sublimate. Unfortunately, the yield from this process is

rather small. It can, indeed, be increased by the addition of some sulphuric acid, but even then there is much room for improvement.

For the purification of crude anthraquinon it has been recommended to boil the crude article with dilute soda-lye and zinc-dust, to filter hot, and to precipitate anthraquinon from the filtrate by blowing in air. This process has the defect that during the filtration a part of the hydroanthraquinon becomes oxidised, and consequently remains in the residues, and that phenanthraquinon also is reduced by zinc-powder and soda-lye. Anthraquinon purified in this manner requires to be treated with sulphuric acid to make it fit for the subsequent operations.

Anthraquinon sublimes in beautiful golden-yellow needles, but on the large scale it is obtained in fine dark gold-coloured columns, several inches in length. The colour varies greatly, depending probably on the size of the crystals. Under certain circumstances, particularly in a state of minute division, it is almost colourless; e.g. if precipitated by water from a solution in sulphuric acid. Even then, however, it is not perfectly colourless, and the golden hue must indubitably rank among its characteristic properties. In ether and benzol it is sparingly soluble, though the latter solvent takes it up more freely at the boiling-point than when cold. Its melting-point is  $273^{\circ}\text{C}$ . Its vapour density was determined experimentally by Graebe as 7.33, whilst, according to the formula  $\text{C}_{14}\text{H}_8\text{O}_2$ , theory would require 7.20. Schützenberger has described an isomeric anthraquinon, which he obtained on repeating the experiments of Graebe and Liebermann. It crystallises in fine red needles, resembling alizarin, from which it is distinguished by its insolubility in caustic alkalis and ammonia. This isomer is transformed into ordinary yellow anthraquinon if its vapour is heated to  $300^{\circ}$ . It is obtained by the action of nitric or concentrated sulphuric acid upon the products of chloride and anthracen.

Auerbach also obtained a red anthraquinon from alizarin paste. If this is evaporated to dryness and sublimed, the sublimate is not perfectly soluble in hydrate of soda; but orange red needles are left behind, completely similar to alizarin in their external properties, but distinguished by their insolubility in caustic alkalis. With zinc-powder and hydrate of soda they give the characteristic red colour of anthraquinon. This red anthraquinon seems to be a compound of anthraquinon and alizarin. If it is treated with benzol, this liquid, on being shaken up with hydrate of potassa, turns violet, whilst the anthraquinon, if treated at once with potassa, shows no colour.

Anthraquinon is distinguished by its stability. It resists the action of oxidising agents with remarkable energy. On fusion with hydrate of potassa it is converted into anthraquinonhydron and anthrahydroquinon.

Bromine has no action in the cold upon anthraquinon, whether dry or dissolved in bisulphide of carbon. On prolonged heating to  $160^{\circ}$  in sealed tubes bibromanthraquinon is formed.

It is less affected by reducing agents than are the quinons of benzol and naphthalin. In behaviour and in formation the quinon of naphthalin takes an intermediate position between those of benzol and of anthracen. Quinon and its chloro-substitution products are readily reduced by sulphurous acid; bichlornaphthaquinon is not altered by this reagent, but is converted into the corresponding hydroquinon on heating with hydriodic acid. Anthraquinon cannot be converted into bioxyanthracen even by hydriodic acid.

If anthraquinon is heated for some hours to  $150^{\circ}$  in a sealed tube along with hydriodic acid (boiling at  $127^{\circ}$ ) and some yellow phosphorus, the yellow needles disappear, and colourless leaflets appear in their stead. These, however, consist not of bioxyanthracen, but of anthracen mixed with a little anthracenbihydride. The reduction of anthraquinon

to anthracen is easily effected with zinc-powder. The transformation succeeds perfectly if the anthraquinon is mixed with ten parts of zinc-powder, placed in a combustion-tube closed at one end, and a layer of zinc-powder filled in at the open end. Heat is then gradually applied to the tube from the front to the back, as in an organic analysis, till a faint redness is reached. The anthracen is deposited in the cold front-end of the tube in pure leaflets. As zinc-powder, when heated alone, yields large quantities of hydrogen in consequence of containing hydrous oxide of zinc, the reduction of anthraquinon to anthracen is intelligible :



Though Graebe and Liebermann stated that anthraquinon resists the action of oxidising agents with extraordinary pertinacity, Wartha succeeded in oxidising it, notwithstanding its remarkable permanence. If an absolute alcoholic solution of pure, almost colourless, anthraquinon (obtained by means of chromic acid, and repeatedly sublimed) is heated to a boil in a test-tube with solid caustic potassa, it is soon found that the liquid turns yellow, and forms two strata—a lower, consisting of melted potassa, and an upper, consisting of an alcoholic solution of anthraquinon. On continued heating the solution becomes darker, and finally, if but little alcohol is present, turns brownish black. The two liquids now mix together with a strong evolution of gas; the mass becomes a fine green, then dark blue, and on continued heating the characteristic violet colour of alizarin-potassa appears. The mixture is now allowed to cool, and dissolved in water; the violet-purple solution is precipitated with sulphuric acid and extracted with ether. From the ethereal solution alizarin, with all its characteristic attributes, can be separated by means of aqueous potassa. In this operation, however, by far the larger part of the anthraquinon is not attacked, and

can be transformed into colouring-matter by repeated fusion with fresh doses of potassa and alcohol.

If stannous chloride is added to the alcoholic solution of anthraquinon, and if it is heated with solid potassa in the same manner to fusion, a peculiar phenomenon is observed. If the chloride of tin is in excess, the lower fused stratum of potassa turns green much sooner than when melted without chloride of tin; the upper alcoholic layer shortly becomes a fiery blood red, and if allowed to cool and to stand uncovered, or if a current of air is passed through, it becomes covered with a brown crust. If this is removed by shaking the liquid, it forms again as long as the fluid displays the intense red colour. The black-brown precipitate deposited, when filtered and washed, can be partially converted into alizarin by solid potassa alone. If the above-mentioned blood-red potassic solution is not allowed to cool, but heated to fusion, the whole mass becomes green, then blue, and finally violet. If an excess of chloride of tin has been added, less alizarin is formed, or sometimes none at all. A small addition of stannous chloride, however, augments the yield of colouring matter. The above-mentioned operations can only be successfully conducted with small quantities. If large amounts are employed, nothing but brown or reddish-brown humus-like bodies are often produced, with little or no colouring-matter. The direct oxidation of anthraquinon can be rendered much more productive by mixing it thoroughly with two parts of sodium-ethylat, and adding it to melting potassa. After the addition of some portions of this mixture there is much frothing, the mass becoming black-brown, and subsequently quite black. The addition is gradually continued, with constant stirring, till the product becomes quite thick, and appears of a blackish-violet in thin layers on the edge of the porcelain capsule. After the mass has been kept at the melting-point for about fifteen minutes, it is allowed to cool; the violet solution is precipitated with sulphuric acid, and

thus the impure colouring-matter is obtained in the form of brown flakes, which are contaminated with undecomposed anthraquinon, as well as with humus-like substances formed during oxidation. It is shaken up with ether, which merely dissolves alizarin and some anthraquinon; the pure colouring-matter is withdrawn from the ethereal solution by means of soda-lye, and the same operations are repeated with the same portion of ether, as long as it takes any colour. The coloured solutions are then mixed together, filtered, washed, dried, and sublimed. The small amount of anthraquinon still adhering to the alizarin may be safely and completely removed by cautiously heating in the sand-bath to  $180^{\circ}$ – $200^{\circ}$ . It is only at higher temperatures, approaching  $300^{\circ}$ , that alizarin sublimes in characteristic orange-red needles.

Gräbe and Liebermann have discovered another method of decomposing anthraquinon. If it is heated in a silver capsule to  $250^{\circ}$  with potassa, the mass soon becomes blue, as if containing alizarin. If, however, water be added, the solution is decolourised, and little is obtained save anthraquinon, which separates out in flakes. If the action is long continued, the anthraquinon is more strongly attacked; on diluting with water, undecomposed anthraquinon is still precipitated, but on adding an acid to the filtrate, there appears a copious colourless deposit, which distils over with the vapour of water, and leaves merely a trace of a brownish colouring-matter (alizarin?). The acid which separates out in a quantity very large in proportion to the anthraquinon is the benzoic, the formation of which, as the only product of the splitting up of anthraquinon, is the more interesting, as rendering it highly probable that the molecule of anthraquinon is resolved into the same equal halves from which anthracen is formed on its synthesis from benzylchloride. If the temperature of the fused mass of potassa and anthraquinon is raised, a point of time is observed when it is covered with a greenish iridescent film. If the mass is then

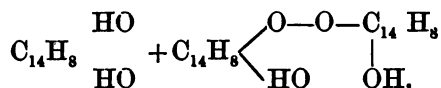
poured into water, the solution takes a splendid cherry-red. On rapid filtration it is found that the filtrate is rapidly decolourised, with the separation of white flakes. If the red alcoholic solution is dropped into an acid, there is obtained a lemon-yellow amorphous precipitate, which quickly changes on exposure to the air, and turns white. The white body produced does not yield a red solution with aqueous potassa, and is insoluble in this reagent. It is anthraquinon.

Care must be taken not to heat the melted potassa too strongly, as otherwise a violent development of hydrogen gas sets in, and the anthraquinon undergoes further decomposition.

This ultimate product has not yet been further examined. The yellow compound which dissolves in alkalis with a red colour can also be obtained by another method, by which its preparation is free from all difficulty, and the nature of the substance is rendered intelligible. If a mixture of anthraquinon and zinc-powder is covered with aqueous potassa, the liquid becomes red even in the cold. The action is completed by heating for a few minutes to 100°, when the anthraquinon is quantitatively transformed. Where the air has access, either anthraquinon or an intermediate compound is separated. The mixture is filtered and precipitated with an acid, air being excluded. The yellow precipitate is placed upon a filter in a current of carbonic acid. The filter is supported by a Plantamour's funnel, in which the precipitate is dried. It dissolves with difficulty in sulphide of carbon. It is soluble in alcohol and ether with a yellow colour and a splendid green fluorescence, but the greater portion is converted into anthraquinon unless the air is excluded. From hot carbolic acid it is obtained in small yellow needles. Concentrated sulphuric acid dissolves it with a violet colour, which changes almost instantly into the ordinary yellow of a solution of anthraquinon in sulphuric acid. Hitherto the quinon-like nature



of anthraquinon had only been inferred from its composition and its direct formation out of anthracen on oxidation, from its behaviour with phosphorus perchloride, and from the fact that on the introduction of two hydroxyls it yields alizarin, which must be unconditionally regarded as a quinon. The proof that an anthrahydroquinon exists—to which anthraquinon bears the same relation as that of quinon to hydroquinon—had previously not been furnished. The above-described compound supplies this deficiency, it being simply anthrahydroquinon or anthraquinonhydron, or probably a mixture of both.



It is possible that the yellow colour of the reduction-product and the red colour of its alcoholic solution may be derived from anthraquinonhydron, and that the anthrahydroquinon itself is colourless.

If the dry product of the reduction is covered with strong potash lye, the surface becomes for a short time a splendid dark-green, probably due to anthraquinon-hydron.

In an alkaline solution anthraquinon-hydron absorbs oxygen, reduces Barreswill's liquid, though the anthraquinon which is separated out at the same time makes the reaction indistinct. The production of this substance on fusion with potassa is easily explained by the reducing action of the hydrogen evolved in the melted mass. It may also be detected, although with greater difficulty as in smaller quantity, on boiling anthraquinon with alcohol, sodium-amalgam, and a little potassa.

*Bibromanthraquinon*,  $\text{C}_{14}\text{H}_6\text{Br}_2(\text{O}_2)$ .

It has been already observed above that bibromanthraquinon can be obtained by two methods. It is formed firstly by the direct action of bromine upon anthraquinon

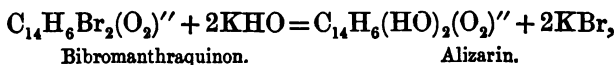
at 160°. The calculated quantities of the ingredients are introduced into a tube, mixed as well as possible—upon which the success of the reaction essentially depends—the tube is sealed and heated in the air-bath until all or nearly all bromine vapours have disappeared, which requires a considerable time. On opening the tube large quantities of hydrobromic acid escape, and the appearance of the contents is found to have become modified. The resulting mass is recrystallised from benzol. This method of preparation is not readily successful, as hard masses are almost always formed, in which a portion of the anthraquinon escapes the action of the bromine.

Bibromanthraquinon may be more conveniently obtained from tetrabromanthracen. One part of the latter is heated with two parts chromate of potash and five to six parts of colourless nitric acid of specific gravity 1·4 in a spacious flask. The reaction is very violent at first; bromine escapes in large quantity, and the liquid sometimes froths strongly.

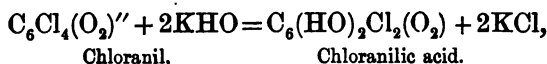
As soon as the development of bromine-vapours ceases, the action is complete. It is then diluted with water; the mass, which has become pale yellow, is collected upon a filter, washed, and recrystallised from benzol. The oxidation succeeds also well with glacial acetic acid and chromic acid.

Bibromanthraquinon crystallises in light yellow needles and sublimes undecomposed in the same form.

It is very sparingly soluble in alcohol, but more readily in benzol and chloroform. It undergoes double decomposition much less easily than the chlorised and bromised quinons of benzol and naphthalin. Potassic hydrate only acts upon it at temperatures above 200°. Alizarin is then formed according to the subjoined equation, and combines with two molecules of potassa to alizarate of potassa :



This reaction corresponds exactly to the production of chloranilic acid from chloranil :

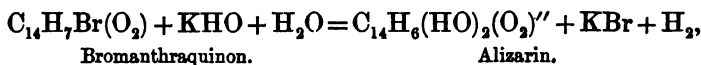
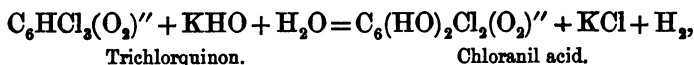


*Monobromanthraquinon*,  $\text{C}_{14}\text{H}_7\text{Br}(\text{O}_2)$ .

This compound is obtained from tribromanthracen exactly as is bibromanthraquinon from tetrabromanthracen.

It crystallises in light yellow needles, melts at  $187^\circ$ , and sublimes undecomposed in needles. It is sparingly soluble in alcohol, tolerably freely in hot, but scarcely in cold benzol. If concentrated along with hydrate of potassa, it is converted, not into the corresponding oxygen compound, but into bioxyanthraquinon—i.e. alizarin, as will be analytically proved below. Monobromanthraquinon behaves in this respect like trichloroquinon, which is converted by alkali into chloranilic acid.

Hydrate of potassa has therefore in both cases a further oxidising action.



*Bichloranthraquinon*,  $\text{C}_{14}\text{H}_6\text{Cl}_2(\text{O}_2)$ .

This compound is obtained in a similar manner to bibromanthraquinon. Tetrachloranthracen is oxidised either by means of glacial acetic acid and chromic acid, or by nitric acid, as described above under bibromanthraquinon.

In its external properties it completely resembles the corresponding bromine compound; it crystallises in yellow needles, and dissolves not very readily in benzol, but more

freely than the corresponding bromine compound. It is sparingly soluble in alcohol and ether.

On fusion with hydrate of potassa it yields alizarin.

*Mononitroanthraquinon*,  $C_{14}H_7(NO_2)O_2$ .

In order to nitrate anthraquinon, it is dissolved with the aid of heat in at least 6 parts, but preferably in 10–12, or even larger proportions of nitric acid of from 1.48 to 1.5 sp. gr., and the solution kept at a brisk boil from 30 to 45 minutes in case of small quantities, or a correspondingly longer time if the quantity is large.

Afterwards the liquid is poured into an excess of cold water, and the pale yellow flakes precipitated are washed with water. The preparation is therefore very simple, but the product is naturally not quite free from quinon. If pure anthraquinon is used, higher oxidation-products are formed, only in very small quantities.

Mononitroanthraquinon, when dried, is a pale yellow, and, like most of the anthraquinon compounds, a very electric powder. At high temperatures it sublimes readily in minute needles, pale yellow, or almost white, which, at 230°, melt to a yellow liquid. It is insoluble in water, scarcely soluble in ether, very sparingly in alcohol, more readily in acetic ether, benzol, chloroform, oil of turpentine, also in glacial acetic acid, from which it crystallises in fine needles, which readily dissolve with a brownish-yellow colour in concentrated sulphuric acid and in aniline, with the latter of which, like the dinitro-compound, it forms a resinoid combination, which dissolves with a rich magenta colour in acetic acid, acetic ether, and other ethereal solvents. It is readily soluble in nitrobenzol, whence it can be obtained in narrow, neat monoclinic columns. If dissolved in concentrated sulphonitric acid, it is readily and completely converted into a dinitroanthraquinon, which is in part at once deposited from the acid solution.

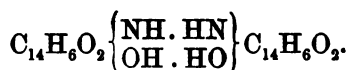
Very remarkable is the behaviour of a mononitroanthraquinon with alkali at a melting heat. Alizarin is produced in abundance, but there is also reproduction of a certain quantity of anthraquinon.

The mononitrated quinon-derivative behaves also like a dinitroanthraquinon when its solution in an excess of common sulphuric acid (12 to 16 parts) is heated to 200°. There is a moderate liberation of sulphuric acid, and the liquid soon takes a deep brownish-red colour. On adding zinc the reaction is similar. When the first action is at an end the mixture is allowed to cool a little, and heated again till the odour of SO<sub>2</sub> has disappeared. It is then poured into cold water, the precipitate of fine violet-red flakes is well washed in cold water, dried, and purified by repeated evaporation from alcohol.

We obtain the compound as a powder, having more or less the colour of peach-blossom. When heated, it melts to a deep cherry-red liquid, from which sublime rose-coloured needles melting at 240°.

It is almost insoluble in water, more soluble in alcohol, ether, acetic ether, chloroform, benzol, and glacial acetic acid, with a deep rose colour, and crystallises very beautifully from the last-mentioned solvent. Concentrated sulphuric acid dissolves it readily with a light brownish-red colour, and hydrate of potassa with a violet red, as does also ammonia, but less readily. Concentrated nitric acid produces an immediate brown colouration, and on boiling there is produced a reddish-yellow solution, from which water precipitates a nitro-compound in bright yellow flocks—easily soluble in potassa—with a vinous red colour, and if melted with this alkali yielding alizarin.

The results of the analysis agree with the formula  $C_{25}H_{16}N_2O_6$ , according to which the compound may be regarded as imidohydroxylantraquinon.



The colouring matter,  $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_4$ , obtained from a dinitro-anthraquinon has been named by Boettger and Petersen a diamidodihydroxylanthraquinon.

On heating ordinary dinitronaphthalin with concentrated sulphuric acid there is formed naphthazarin, the nitrogen-groups of the nitro-compound being simply put aside. That in the analogous and mononitroanthraquinon, just as in a dinitroanthraquinon, they are merely changed, and no new dioxy-grouping is produced, is easily intelligible, since the latter is already present.

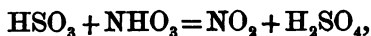
*Dinitroanthraquinon*,  $\text{C}_{14}\text{H}_6(\text{NO}_2)_2(\text{O}_2)''$ .

This compound was discovered by Fritzsche, and was named by him oxybinitrophoten or 'reagent.' Its formation from anthracen on treatment with nitric acid and its formula, show that it must be regarded as dinitroanthraquinon.

It is a constant accompaniment of anthraquinon when prepared by boiling anthracen with nitric acid. To obtain it pure and in larger quantities, pure sublimed anthraquinon is treated with about 16 parts by weight of a mixture of equal volumes of concentrated nitric acid (1.5 sp. gr.) and common oil of vitriol. It is heated to about  $40^\circ$ , and the action is completed by a short ebullition. As soon as the solution appears clear it is poured into excess of cold water, when dinitroanthraquinon is deposited in yellowish-white flocks.

It is also obtained if anthraquinon is treated with nitrosulphuric acid, or if the bisulphanthraquinonic acid obtained by heating anthraquinon with sulphuric acid is treated with nitric acid.

The sulphuric acid group is here eliminated by nitric acid and replaced by the residue  $\text{NO}_2$ :



a reaction which has been repeatedly observed of late.

Graebe and Liebermann describe the dinitro-product thus obtained as isobinitroanthraquinon. No fewer than sixteen isomeric dinitroanthraquinons are theoretically possible.

The dinitroanthraquinon prepared by means of nitric and sulphuric acids was named *α*-dinitroanthraquinon by Anderson and Fritzsche.

This compound is almost insoluble in water, scarcely soluble in ether, very sparingly soluble in alcohol and benzol, and rather more freely so in chloroform, from which it may be obtained in small, granular, pale yellow microscopic crystals. The precipitated flocks yield when dry a light, pale yellow powder, somewhat sensitive to light.

When heated, the compound turns brown, clots together at 252°, and at higher temperatures sublimes in small brownish, generally rather dull acicular crystals, a considerable portion being decomposed and carbonised. If rapidly heated in a flame it burns quietly away, the separation of carbon being not very great. The larger crystals, whether obtained by sublimation or from solvents, appear under the microscope as monoclinic prisms with domal terminal planes, frequently bent or grouped together like the teeth of a saw, cruciform or aggregated in forked twin crystals. It is not affected by concentrated alkaline solutions, but on fusion with alkali a brown humus-like body is formed with partial carbonisation, a small quantity of alizarin is formed, ammonia escapes, and a gas which causes a smouldering chip of wood to glow more vividly.

Reducing agents convert it into diamidoanthraquinon.

If dinitroanthraquinon is boiled for some time with anilin, it dissolves, the liquid takes a red colour and dissolves in excess of water. If the liquid is mixed with hydrochloric acid, it turns first to a dirty yellowish brown, but on the

addition of more acid to a fine magenta, black resinous flocks being deposited. These flocks are insoluble in water, alkali, and alcohol, but dissolve readily in bisulphide of carbon with a splendid magenta colour. If the sulphide of carbon is shaken up with water, the red colour is not withdrawn; alcohol also takes up very little of it, and deposits a yellow powder on the addition of carbonate of soda. If silk is dyed with the aqueous solution of the colouring matter before treatment with acid, it takes a rose shade, which on washing passes into a dull yellow.

On concentrating dinitroanthraquinon in the water-bath along with a strong solution of potassic cyanide, the residual mass becomes a dark-red violet. If heated in the sand-bath we obtain a fine vermilion sublimate, whilst the mass tumefies and smoulders. If the black residue is extracted with water, a dark-red solution is obtained, from which dark-brown flocks are separated on prolonged standing, whilst a carbonaceous mass insoluble in water is left behind.

On treatment with concentrated sulphuric acid, dinitroanthraquinon yields a violet dye. To obtain it, dinitroanthraquinon is dissolved in an excess of oil of vitriol and heated in the sand-bath. At about  $200^{\circ}$ , a moderate escape of sulphurous acid sets in, and the solution turns from a yellowish brown to a reddish brown. The mass is then thrown into cold water, washed repeatedly, dissolved in dilute alkali and reprecipitated with acid, and finally obtained from an alcoholic solution by slow evaporation. There remains a black humoid mass and a small quantity of an analogous dye, more blue in colour and sparingly soluble in alkalis.

This violet dye may be likewise obtained by treating anthraquinon with excess of sulphuric acid and a little nitric acid. It dissolves in water with the colour of peach-blossom; is readily soluble in alcohol, ether, acetic ether, chloroform, sparingly in benzol with a splendid violet-red colour, and on slow evaporation crystallises out in violet



granules. On rapid evaporation, especially from alcohol, it is obtained in violet-brown crusts, iridescent like certain cetonæ. Concentrated acetic acid dissolves it with a fine magenta red, but concentrated sulphuric acid with a hyacinth red colour. On heating, it melts to a violet-red liquid, and sublimes but partially in violet crystals, being chiefly carbonised. According to analysis its formula is  $C_{14}H_8N_2O_4$ . It dyes cotton without a mordant, and on treatment with hydrate of soda evolves ammonia.

On a further study of this violet dye Petersen pronounces it a diamidohydroxylanthraquinon, a constitution which explains its great tinctorial power, as (namely in dihydroxylanthraquinon, which already possesses tinctorial power) a nitrogen-group poor in hydrogen is present, which generally further heightens this power. But if the diamido-groups are linked together, the two nitro-groups of dinitroanthraquinon from which they have arisen must have been adjacent to each other.

If into the alcoholic-ethereal solution of  $C_{14}H_8N_2O_4$  there is passed a current of nitrous acid (ether is used to economise alcohol, which eagerly absorbs nitrous acid), the intense violet liquid is gradually decolourised and becomes finally a light brown, whilst some deep-brown flocks and granules separate out. The ether and a part of the alcohol are expelled by heat, and the solution thus concentrated is poured into an excess of water, where resinous flocks, deep yellow or orange coloured, are deposited and dried over sulphuric acid, as they easily clot together if heated. They readily melt to a red-brown liquid, which, on cooling, forms a brown vitreous mass, brittle and somewhat transparent. At higher temperatures the compound sublimes, giving out a peculiar saffron odour, which at the same time is suggestive of anthraquinon, and forming fine yellow or faint hyacinth-red flat and apparently orthorhombic needles in feathery groups and twig-like ramifications, or leaflets of a vitreous lustre with a greenish-

yellow surface-reflection. These soften at  $142^{\circ}$ , but are slow in coming to full fusion. They are insoluble in water, readily soluble in alcohol, especially if hot, less soluble in ether, and with a yellow colour. In concentrated sulphuric acid they dissolve with a bright orange colour, and in caustic alkali with a raspberry red. On standing, bright red flocks are deposited. On fusion with hydrate of soda, alizarin is readily formed. The analysis of this compound leads to the formula  $C_{14}H_7NO_8$ , and it has received from Petersen the name oximidodihydroxylantraquinon. If dinitroanthraquinon is heated only for a short time with concentrated sulphuric acid till the solution takes a brown colour, and sulphurous acid is evolved after cooling, small short light yellow columnar crystals are formed, which are possibly  $\alpha$ -dinitroanthraquinondisulphuric acid,  $C_{14}H_4(NO_2)_2(SO_3H)_2O_2$ . The two sulphuric acid residues would here occupy the positions 6 and 7, i.e. that of alizarin.

The ease with which oximidodihydroxylantraquinon or  $\alpha$ -oximidoalizarin is obtained from the above-described compound makes the presence of the two hydroxyls in the violet dye very probable.

*Monoamidoanthraquinon,  $C_{14}H_7(NH_2)O_2$ .*

Mononitroanthraquinon can be amidised by means of reducing agents, as readily as the dinitro-compound. It is best to employ sodium sulphydrate. Finely pulverised mononitroanthraquinon is heated with a moderately concentrated aqueous solution of the sulphy-salt. The liquid takes at first a green colour, but not as bright as when dinitroanthraquinon is employed. It then turns violet, whilst flocks of a more or less decided red colour are deposited. It is kept for a time at a boil, diluted with water, allowed to cool in order to keep as little amid as possible in solution, filtered and washed with cold water. The  $\alpha$ -monoamidoanthraquinon

thus obtained and dried appears, when pure, as a bright brick-red powder, which can be easily obtained by sublimation in rhombic acicular crystals of the same colour. The vermilion powder of  $\alpha$ -diamidoanthraquinon, on the other hand, sublimes in fine flat garnet-red needles with a greenish reflection; melting point  $256^{\circ}$ . The compound is sparingly soluble in alcohol and ether, more freely in acetic ether, chloroform, benzol, and glacial acetic acid, from which it may be obtained in beautiful crystals. It dissolves in concentrated sulphuric acid with a brown-red colour. Acid compounds do not seem to be formed.

This substance, if melted with potassa and treated with water, displays a deep blue-violet colour, but the product precipitated from it by acids contains a little alizarin.

*Diamidoanthraquinon*,  $C_{14}H_6(NH_2)_2O_2$ .

This compound was discovered by Boettger, and was named by him anthracen-orange. It is a reduction product of dinitroanthraquinon, from which it can be produced in various ways.

It is obtained by treating dinitroanthraquinon with zinc and hydrochloric acid, or potassa lye. Boettger gives the following directions:

Dinitroanthraquinon is covered with a solution of stannite of soda. A splendid emerald green solution is at once formed, from which, on heating to a boil, diamidoanthraquinon separates out in beautiful vermilion flocks. These are filtered, well washed with water, dried, and sublimed. Instead of stannite of soda, sodium sulphide, or preferably ammonium sulphide, may be used. The latter especially effects the reduction very easily. The dinitroanthraquinon is covered with yellow sulphide of ammonium, and heated to a boil, when the red flocks are obtained in abundance.

In preparing diamidoanthraquinon with stannite of soda,

a stanniferous product is often obtained, which precipitates in heavy violet flocks. These dissolve very readily in alcohol with a violet colour. Acids turn them red, and alkalis restore the violet colour. They dye wool, silk, and cotton directly, but the shades are faint and dingy.

Diamidoanthraquinon sublimes readily and without much carbonisation. After it has melted to a deep cherry-red liquid—which, if allowed to cool, shows a green surface reflection—there sublime splendid greenish-red fine flat needles often forming plumose groups, with a greenish surface reflection. Under the microscope they appear as rectangular, probably rhombic, crystals (the two vertical pinacoids with the terminal plane). They melt at  $236^{\circ}$ , but sublime at a lower temperature.

*a*-diamidoanthraquinon dissolves very slightly in water, not very freely in alcohol, wood-spirit, ether, aldehyd, acetone, somewhat more abundantly in acetic ether, rather freely in chloroform, glycerin, and benzol, and less readily in disulphide of carbon.

The solutions vary from a hyacinth to a raspberry red. From the ethereal solutions it may be obtained in small crystals. Concentrated sulphuric acid dissolves it with a brown yellow colour, but on dilution with water it is separated unchanged in red flocks; it is but slightly soluble in dilute sulphuric, hydrochloric, and nitric acids. From these solutions the compound is gradually deposited in a pulverulent form. This amid has a feebly basic character. If we attempt to pulverise diamidoanthraquinon when perfectly dry in a porcelain capsule, every particle becomes so strongly electric, and adheres so firmly to the capsule, that it cannot be removed without loss.

If melted with hydrate of soda, it yields alizarin. C. Liebermann, however, has observed that the colouring matter thus produced has a violet colour tending more to blue, and on exposure to the air and on sublimation deviates in some

respects from ordinary alizarin. The same compound was prepared by Liebermann from the product obtained from the action of nitrous acid upon binitroanthraquinon by fusion with hydrate of soda. If the same product is merely boiled with aqueous potassa, a yellow solution is obtained, so that we must assume a mere partial transformation of the groups  $\text{NO}_2$  of nitrous acid.

If the emerald green solution produced on adding stannite of soda to the nitro-compound of anthraquinon, instead of being heated, is mixed with an excess of dilute sulphuric acid, there appears a flocculent brown precipitate, which, if washed, dried, and dissolved in alcohol, leaves, when the alcohol is distilled off, a brown colouring matter, which, if dissolved in acetic ether or alcohol, gives a deep reddish-purple liquid.

#### *Azo-compounds of Anthraquinon.*

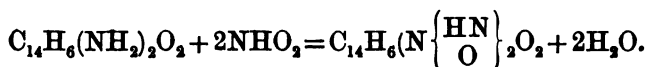
These compounds have been chiefly studied by Anderson and Fritzsche. They are formed from diamidoanthraquinon when its alcoholic solution is treated with nitrous acid.

If the acid aqueous solution of diamidoanthraquinon is treated with nitrous acid, no azo-compound is found; but the case is different if the alcoholic solution is treated with this acid. The hyacinth-red solution becomes first violet, then brownish-yellow; and if then mixed with water, yellow flocks are separated, which are merely regenerated anthraquinon. It is better, therefore, to use an alcoholic solution. On passing into it nitrous acid a brownish-violet powder is deposited, which dissolves in water and alcohol with a violet colour. The aqueous solution, if boiled, or allowed to stand open to the air without heat, yields diamid along with products of decomposition without any evolution of nitrogen.

The compound, which, according to its analysis, has the formula  $C^{14}H^6N^4O^4$ , may be regarded as



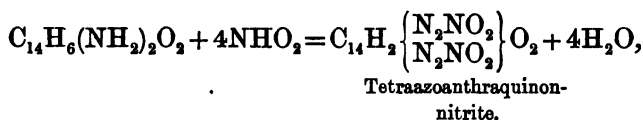
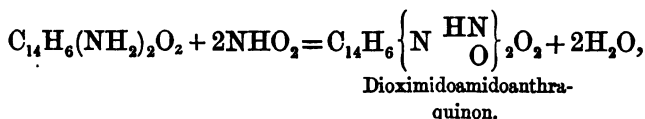
It may be regarded as a diamidoanthraquinon twice combined with the group  $N\begin{smallmatrix} H \\ ON \end{smallmatrix}$ , or, according to the experiments of Graebe and Liebermann on certain naphtha-compounds, as dioximidoamidoanthraquinon with the group  $N\begin{smallmatrix} O \\ HN \end{smallmatrix}$  twice repeated, when the following expression may be given to the reactions :



Dioximidoamidoanthraquinon is probably the first product of the reaction of nitrous acid upon diamidoanthraquinon. At the same time there is produced more or less of a brown, strongly explosive azo-compound, which does not dissolve in water with a violet colour, but with frothing and escape of nitrogen gas, and dissolves in potassa with a brown colour. If melted in potassa it yields alizarin, and can be obtained almost pure from diamid if dissolved in chloroform, in which it is far more soluble than in ether and acetic ether, whence the action of nitrous acid upon such a solution is far more energetic. The analyses of Boettger and Petersen agree with the formula



The formation of both these azo-compounds would therefore take place in accordance with the following formula :



The still more violently explosive compound, which hitherto has been only obtained once, is probably



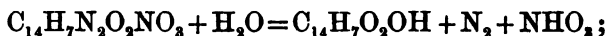
Generally speaking, the nitrogenous derivatives of aromatic bodies rich in carbon are far more manifold than those of such as are poor in the same element.

*a-Diazoanthraquinonnitrate*,  $C_{14}H_7N_2O_2NO_3$ .

If a current of nitrous acid is passed into the solution of the monamid in ethylic ether, the solution is decolourised after some time, and there falls a powder, pale, red, or sulphur yellow, of the composition above mentioned. The solution of the amid in acetic ether is gradually turned brown by nitrous acid without any precipitation. From the solution in chloroform is obtained a brown substance, not adapted for closer examination.

This azo-compound dissolves sparingly in water with a reddish colour, which, in contact with caustic potassa, becomes immediately pale brown. It is much more soluble in alcohol and acetic ether; insoluble in ether. If heated with water, nitrogen gas is evolved in abundance, whilst yellow or brown flocks are deposited, and the liquid has an acid reaction due to free nitrous acid. The flocks, after

filtration and drying, sublime, when heated in shining flat needles or lamellæ, lemon yellow or gold coloured, which display the reactions of oxyanthraquinon. The melting-point is about  $202^{\circ}$ . The transformation of the diazo-compound into the hydroxylate ensues according to the equation



whilst the azotised product obtained from the diamid is only converted into alizarin on fusion with potassa. The azo-compound is moderately permanent, but it gradually gives off nitrous vapours, and, if heated, deflagrates slightly, leaving a carbonaceous residue.

*Methylantraquinon*,  $\text{C}_{15}\text{H}_{10}\text{O}_2$ .

This compound is obtained by the oxidation of methyl-anthracen in an alcoholic solution, and melts at  $162^{\circ}$ – $163^{\circ}$ .

It dissolves with moderate readiness in ether, acetone, chloroform, and boiling alcohol; sparingly in glacial acetic acid and benzol. From these solvents it separates in crystals or in minute yellow needles. If heated with zinc powder and soda lye it yields Liebermann's reaction for anthraquinon. If methylantraquinon dissolved in sulphide of carbon is placed in a sealed tube with bromine and heated for some hours in the water-bath, the result is a finely crystallised bromine compound, which, if fused with caustic potassa at  $180^{\circ}$ – $200^{\circ}$ , yields a dye resembling alizarin. It is best obtained from the sulpho-acid. For this purpose methyl-anthraquinon is heated with five or six parts of fuming sulphuric acid to  $250^{\circ}$ – $270^{\circ}$  for several hours; the liquid, before it is quite cold, is poured into water and neutralised with carbonate of baryta or lime; the sparingly soluble baryta or lime salts are repeatedly extracted with boiling water, and the sulphate of baryta or lime is removed by filtration.

The solutions of the baryta or lime salts are decomposed



with carbonate of potash, and the filtered solution of the potash salt is evaporated to dryness. If the salt thus obtained is melted with excess of potassa at  $200^{\circ}$ , the mass soon displays the colour phenomena of an ordinary alizarin melt. Acids precipitate the colouring matter in yellowish-brown flocks. It is best purified by sublimation. It sublimes when heated above  $200^{\circ}$  in red tufts, or it is repeatedly recrystallised from alcohol and aceton, and thus obtained pure. Methylalizarin dissolves in alkalis with a blue violet colour. With salts of lime and baryta, it forms blue precipitates. The melting-point is from  $250^{\circ}$  to  $252^{\circ}$ . Methylalizarin dyes cotton mordanted with iron or alumina in shades closely resembling those produced by alizarin. Kundt, in his spectroscopic examinations, was unable to find any essential difference between methylalizarin and common alizarin. It is therefore for the present doubtful whether the methylalizarin did not contain an admixture of ordinary alizarin, which might easily occur during the fusion with potassa by abscission of the methyl group.

#### *Sulphanthraquinonic Acids.*

These acids were first described by Graebe and Liebermann along with Caro, and were obtained by these chemists on heating anthraquinon with sulphuric acid to  $260^{\circ}$ . They observed subsequently that the sulphanthraquinonic acids can be directly prepared from anthracen by dissolving it in sulphuric acid, and treating the sulphanthracenic acid with oxidising agents such as chromate of potash, nitric acid, or manganese, whereby the sulphanthracenic acid is converted into the sulphanthraquinonic. According to Auerbach, sulphanthraquinonic acid may also be obtained by heating anthracen with sulphuric acid to  $212^{\circ}$ , when  $\text{SO}_2$  is given off, and the anthracen is oxidised to anthraquinonic acid. The two latter methods have, however, several disadvantages.

They require, in the first place, a very pure anthracen, since, if an impure quality is used, the impurities are also converted into sulpho-acids, which can scarcely be separated from the sulphanthraquinonic acid, and which, on further treatment and conversion into alizarin, contaminate this also. In the second place, isomeric sulpho-acids seem to be formed, which, when melted with alkali, do not yield alizarin. Thirdly, even if chemically pure anthracen is employed, the respective preparation of the blue and the red shades of alizarin is not under control, since a mixture of the two sulpho-acids is always produced, and no homogeneous acid can be obtained in this manner on the large scale. The only practical method for obtaining the sulpho-acids is the one first mentioned, with anthraquinon and sulphuric acid, preferably fuming.

According to circumstances—i.e. the higher or lower temperature, the larger or smaller proportion of acid, there is formed the mono- or the bisulpho-compound. If 1 part of anthraquinon and 3 parts of concentrated sulphuric acid are heated to about  $260^{\circ}$  till all anthraquinon has disappeared, and none consequently is separated on the addition of water to a portion taken out, we obtain a mixture of both acids. The one or the other predominates according as the heat has been applied for a longer or shorter time, and has reached a higher or lower degree. It has not yet been found practicable to show whether isomeric sulpho-acids are formed during the process.

The preparation of the several acids on the small scale is somewhat difficult. The mono-acid is found to predominate if anthraquinon is used in excess, and the mixture is heated to  $250^{\circ}$ – $260^{\circ}$ . The bi-acid is obtained on using sulphuric acid in excess and heating to  $270^{\circ}$ – $280^{\circ}$ .

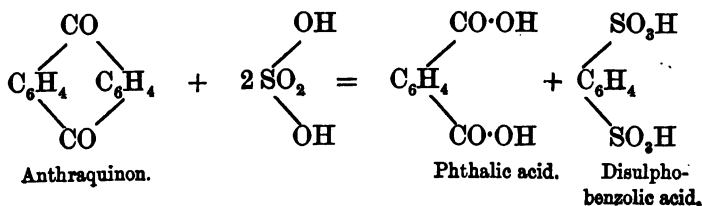
As both acids are but sparingly soluble in sulphuric acid, the mixture solidifies in both cases when the reaction is complete and it is allowed to cool. A considerable amount

of water and a prolonged digestion are required to redissolve the whole. It is therefore advisable to pour the mixture cautiously into water before it is quite cold. From this solution calcium, barium, and lead salts may be obtained by known methods. The barium salts, on account of their sparing solubility in water, are well adapted for the isolation of the acids in experiments on the small scale. For large quantities the lime salts are used for separation from the excess of sulphuric acid.

Weith and Bindschädler obtained phthalic acid as a bye-product during the formation of the sulpho-acids. It was produced when anthraquinon, purified by recrystallisation from sulphuric acid, was heated to 270° with 3 to 4 parts of fuming sulphuric acid.

In order to place the formation of phthalic acid beyond doubt, they made the experiment with chemically pure anthraquinon, perfectly free from phthalic acid. This was heated for six hours to 270° with 4 parts of fuming sulphuric acid. Sulphurous acid was given off, and there sublimed colourless needles, an inch in length, which, from their melting-point (129°) and other properties, were found to be anhydrous phthalic acid. They dissolved in hot solutions of carbonate of soda, and on addition of acid and agitation with ether pure phthalic acid was obtained, with its characteristic properties. Their amount was 8 to 9 per cent. of the anthraquinon employed.

This formation shows that anthraquinon is a keton of phthalic acid, and the latter may have been formed according to the following equation:—



Disulphobenzolic acid, or the dioxybenzol formed from it on melting—pyrocatechin according to Baeyer's researches—should be found in the mother-liquors of alizarin.

This formation of phthalic acid, however, only occurs if the preparation of the sulpho-acids is not properly conducted. Where the experiment is successful no phthalic acid appears.

*Monosulphanthraquinonic Acid*,  $C_{14}H_7(SO_3H)O_2$ .

The pure acid is obtained from the barium or lead salt by accurate precipitation with sulphuric acid and concentration of the solution, when it separates in the form of yellow leaflets. A small quantity of sulphuric acid present in the solution is not injurious, as it diminishes the solubility of the compound in water. In hot water it deliquesces; in cold it dissolves more sparingly, but still readily. From a saturated solution it is thrown down on the addition of sulphuric or hydrochloric acid. Its salts are somewhat sparingly soluble in water.

*Sodium Salt*,  $C_{14}H_7O_2(SO_3Na)$ .

It forms fine silvery leaflets, which dissolve in water with a yellow colour. In hot water it dissolves more freely, but sparingly in cold.

100 parts water at 100° C. dissolve 18.88 parts,

100     "     "     18° C.     "     5.59     "

of monosulphanthraquinonate of soda.

*Lime Salt*,  $[C_{14}H_7(O_2)SO_3]_2Ca$ .

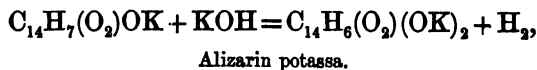
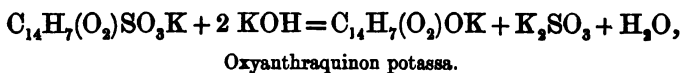
It is much more soluble in water than the baryta salt, but not much more plentifully at 100° C. than in the cold. It forms only indistinctly developed crystals.

*Baryta Salt*,  $[C_{14}H_7(O_2)SO_3]_2Ba$ .

It forms indistinctly developed yellow crystals, which,

under the microscope, appear as tables. In cold water it is very sparingly soluble; more freely, but still slightly, at a boil. The addition of hydrochloric acid diminishes the solubility.

If the potassium or sodium salt of monosulphanthraquinonic acid is heated with caustic potassa or soda, the colour, which is at first red, passes into violet. If the heat is strong enough and sufficiently prolonged, the aqueous solution has the characteristic properties of alizarate of potassa, and acids precipitate alizarin from the solution. If the heat is lower, and if less alkali is used, or if indifferent salts, e.g. elutriated chalk, be added, the resulting solution is rather red than violet, and acids cause the separation of oxyanthraquinon which will be described below. On careful melting, the two successive reactions may easily be observed. There is first formed monooxyanthraquinon, the hydroxyl compound corresponding to monosulphanthraquinonic acid. On further fusion with potassa this is converted by its oxidising influence into bioxyanthraquinon—i.e. alizarin. The true reactions cannot, however, be sharply discriminated. The following equations explain the process:—



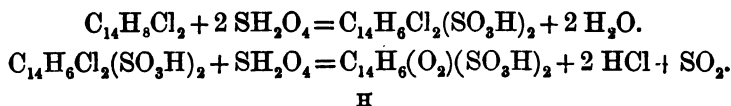
Free hydrogen, however, does not seem to appear. It either exerts a reducing action upon the oxyanthraquinon or upon the sulpho-acid not yet attacked and forms anthraquinon, which is often found in alizarin, or it reduces the alizarin to hydroalizarin, which then during fusion or during solution in water is reoxidised to alizarin by the oxygen of the air.

*Bisulphanthraquinonic Acid,  $C_{14}H_6(O_2)(SO_3H)_2$ .*

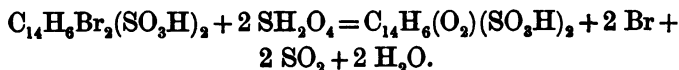
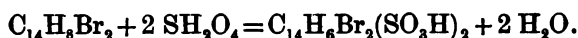
This acid is obtained like the above-described mono-acid, and separates out on evaporating the aqueous solution in yellow crystals much more soluble than those of monosulphanthraquinonic acid. In sulphuric acid it is sparingly soluble, and the mixture of anthraquinon and sulphuric acid used in its preparation congeals therefore on cooling. Its salts also are more soluble than those of the mono-acid. The barytic salt is among the least soluble, whence, independently of the cost, it is more suitable to use the lime salt for separating the product from the excess of sulphuric acid. The salts in the solid state are light yellow, but a yellowish red when in aqueous solution. The solutions of the alkaline compounds are redder than those of the other metals.

Bisulphanthraquinonic acid is formed also on heating bibrom- and bichlor-anthracen with sulphuric acid, which effects at once the formation of the sulpho-acid and the replacement of the atoms of bromine and chlorine of oxygen. At the same time there are formed bromiferous and chloriferous intermediate products, which have been subjected to a closer examination by Perkin. On treating bibrom- and bichlor-anthracen with sulphuric acid, sulpho-acids are formed even in the cold. Concerning these, Perkin has shown that they have the composition of bisulphobibromanthracenic acid,  $C_{14}H_6Br_2(SO_3H)_2$ , and of bisulphobichloranthracenic acid,  $C_{14}H_6Cl_2(SO_3H)_2$ . These are converted by the action of sulphuric acid into bisulphanthraquinonic acid, the chlorine escaping as hydrochloric acid, and the bromine in the free state. The equations showing the formation of bisulphanthraquinonic acid are therefore best resolved into groups of two:—

For bichloranthracen we have,



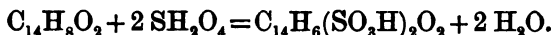
The following equations correspond to bibromanthracen :



The bromine and chlorine compounds dissolve in cold sulphuric acid, at first with a splendid green colour, which in a few seconds becomes a fine magenta. Water, however, precipitates the bromine and chlorine compounds unchanged. On the application of heat the colour disappears, the bromine compound emits red vapours of bromine, the chlorine compound gives off fumes of hydrochloric acid, and the solution then contains bisulphoanthraquinonic acid.

Another method for preparing bisulphoanthraquinonic acid sets out with first preparing bisulphoanthracenic acid, and subsequently oxidising. To obtain it by this method, 1 part by weight of anthracen is heated for some hours to 100° C. with 4 parts by weight of sulphuric acid of spec. grav. 1.848. The temperature is raised to 150°, and kept up for an hour. When cool it is diluted with 3 parts of water, and to 1 part of the anthracen used 2 to 3 parts of manganese are added, and the whole boiled for some time. To complete the process the mixture is concentrated or even evaporated to dryness. The sulphuric acid is neutralised with lime, an excess of which is used to precipitate the manganese, and carbonate of potassa or soda is added to the filtrate until all the lime is precipitated. In place of manganese other oxidising agents may be used, such as peroxide of lead, chromic acid, or nitric acid. If chromic acid is employed, the portion of it not reduced must be converted into chromic oxide before the addition of the lime by means of sulphurous acid. If nitric acid is used, the oxidising mixture is concentrated until the greatest part of the nitric acid is driven off.

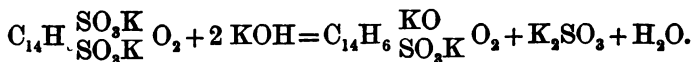
C. Liebermann prepared disulphanthraquinonic acid from  $\beta$ -benzoyl-benzoic acid. If the latter is heated for some time with sulphuric acid till water no longer produces a precipitate, it is converted into bisulphanthraquinonic acid. The reaction takes place according to the equations—



The baryta salt,  $C_{14}H_6(O_2)[SO_3]_2Ba$ , is obtained from water in imperfectly developed yellow crystals, and dissolves sparingly in cold water, but rather more freely at a boil.

The lead salt,  $C_{14}H_6(O_2)[SO_3]_2Pb$ , forms, like the baryta salt, imperfectly developed yellow crystals, and dissolves slightly in cold but more freely in boiling water.

Bisulphanthraquinonic acid, if heated with hydrate of potassa or soda, yields isopurpurin; but here also an intermediate compound may be observed, and indeed much more easily than in the monosulphuric acid. At first only one of the residues of sulphuric acid is replaced by hydroxyl, and there is formed the potassium salt of a sulphoanthraquinonic acid:



On further heating, the other residue of sulphuric acid is substituted; but at the same time a hydrogen is replaced by a hydroxyl, forming a mixture of dihydroxylanthraquinon and isopurpurin. If the action of the hydrate of potassa is sufficiently prolonged, most of the dihydroxylanthraquinon is converted into isopurpurin, of which the final product chiefly consists, with a mere admixture of dihydroxanthraquinon. Which of the three products hitherto found in isopurpurin—i.e. in *alizarin for reds*—namely, anthraflavic acid, isoanthraflavic acid, anthraxanthic acid, is derived from the ordinary disulphanthraquinonic acid is not demonstrated with cer-



tainty. It is certain, however, that none of these three compounds forms alizarin when heated with potassa. This property belongs solely to oxyanthraquinon, which, from its similarity to anthraflavic acid, is often confounded with the latter.

The successive exchange of the sulphuric acid residues for hydroxyl is very well to be seen by the change of colour in the mass. If bisulphanthraquinonate of soda is gradually heated with caustic soda, the original red colour of the melt gradually passes into a deep blue. This blue colour is derived from the soda salt of sulphoxyanthraquinonic acid; and the more this is converted into isopurpurin, the more this colour passes into a reddish violet.

This is best observed by taking out proofs from time to time, and mixing them with a little water upon a white plate. If an acid is then added, it will be found that in the first stage, as long as the mass dissolves with a blue colour, sulphurous acid is evolved, but no precipitate appears. When the reaction is more advanced, and the blue colour is changed into a reddish-violet, yellowish-red flocks of isopurpurin are separated on the addition of an acid, whilst the evolution of sulphurous acid becomes more copious. This is easily explained by the fact that sulphoxyanthraquinonic acid is readily soluble in water. Whether during the fusion important quantities of this intermediate product are present in the mass along with isopurpurin may be ascertained as follows. A trial sample of the melt is taken out and mixed with sulphuric or hydrochloric acid, and shaken with ether. This dissolves the isopurpurin readily, but leaves the sulphoxyanthraquinonic acid behind, which may then be recognised by the blue colour which it produces with alkalis.

On melting the sulphanthraquinonic acids with alkali, along with the principal reaction just mentioned, there occurs to a small extent an exchange of the sulphuric acid residues with hydrogen. Hence anthraquinon sublimes from

the mass. This retroformation of anthraquinon from the sulpho-acids explains in a satisfactory manner the origin of benzoic acid, which is sometimes found in artificial alizarin.

The melting alkali decomposes anthraquinon into benzoic acid as already stated.

The exchange of sulphuric acid residues for hydrogen can be abundantly effected, if the sulphoanthraquinonic acids are heated with lime instead of caustic potassa. From the heated mass anthraquinon sublimes in large quantities.

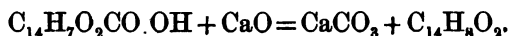
*Anthraquinonmonocarbonic Acid,  $C_{14}H_7O_2CO\ OH$ .*

If methylantracen is dissolved in glacial acetic acid and boiled with chromic acid, there is formed anthraquinonmonocarbonic acid. By recrystallisation from glacial acetic acid it is easily obtained pure as a yellow crystalline mass. It sublimes without residue in yellow crystalline needles, perfectly resembling those of anthraquinon. Its melting-point is  $283^\circ$ .

It is very sparingly soluble in glacial acetic acid, methylic alcohol and absolute alcohol, and almost insoluble in hydrocarbons, such as petroleum, benzol, toluol, as well as in chloroform and ether, but readily soluble in acetone. Concentrated sulphuric acid dissolves it even in the cold, and very readily at a gentle heat, with a yellow colour. On the addition of water the solution is decolourised, with formation of a white flocculent precipitate.

With zinc-powder and soda-lye, anthraquinoncarbonic acid yields the red colouration characteristic of anthraquinon.

If heated with soda-lime to about  $300^\circ$ , it passes into anthraquinon. The mass takes a violet colour, and yellow needles sublime in the anterior part of the tube, which after repeated sublimation have the constant melting-point  $272-273^\circ$ . The reaction takes places according to the equation:



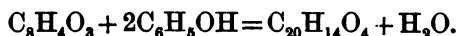
On fusion with caustic potassa, anthraquinoncarbonic acid exhibits changes of colour similar to those of ordinary anthraquinon. At 180-200° the melt becomes a blue-violet, which passes first into red-violet and then into red.

*Oxyanthraquinon*,  $C_{14}H_7(OH)O_2$ .

This compound was first observed by Glaser and Caro as a bye-product of the manufacture of alizarin, and was then more closely examined by Graebe and Liebermann. On analysis it was found to contain an atom of oxygen less than alizarin. Its behaviour, as described below, and its origin place it beyond doubt that it is monohydroxylised anthraquinon. As already stated, it is formed by melting monosulph-anthraquinonic acid with hydrate of potassa, as a direct product of the reaction, and only passes into alizarin on further heating. Since alizarin is formed from the sulph-anthraquinonate of soda, the presence of oxyanthraquinon in a product met with in trade as alizarin of a 'blue' tone is intelligible, whilst in the kind known as yellowish or 'scarlet' (isopurpurin) anthraflavic acid, a compound described below predominates. It is still possible that oxyanthraquinon, under certain circumstances, may be formed from the bisulpho-compound, since, as has been shown above, there is produced by the action of the alkali along with alizarin, a small quantity of anthraquinon, and in consequence of a similar reaction there is formed from the bisulpho-acid a monosulpho-compound which then passes into oxyanthraquinon.

Oxyanthraquinon is also formed from monobromanthraquinon, when melted with potassic hydrate at the lowest possible temperature. It has also been formed synthetically by Baeyer and Caro by the action of phthalic acid upon phenol. If phenol is gently heated with anhydrous phthalic acid and concentrated sulphuric acid, the liquid becomes

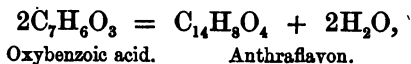
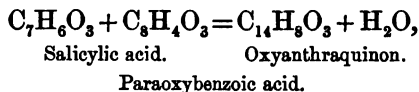
reddish yellow with formation of phenolphthalein, which, on addition of a sufficient quantity of sulphuric acid, passes into sulphophenolphthaleic acid. If a stronger heat is applied the colour disappears, and is succeeded, first, by a deep red, and then by a brownish yellow, which increases with the duration of the reaction and the height of the temperature. On the addition of water, flocks are deposited, yellow or brown, which, when washed, behave like monooxyanthraquinon. The formation of phthalein does not seem here essential, since phenol, if added to a mixture of phthalic acid and sulphuric acid at a sufficient heat, shows the same behaviour without any preliminary formation of phthalein. Since sulphophenolic acid, disulphophenolic acid, and oxysulphobenzid yield an analogous result, we may assume that phenolphthalein, when heated with sulphuric acid, is resolved into phthalic acid and a sulpho-acid of phenol, which bodies at higher temperatures gradually coalesce into oxyanthraquinon, the sulpho-group being replaced by phthalic acid. These reactions are represented by the following equations :



Anisol behaves like phenol, the methyloxy group being transformed into the hydroxyl group. Even anisic acid yields oxyanthraquinon with abscission of the carbonic acid and of the  $\text{CH}_3$  group. Less remarkable is the origin of oxyanthraquinon from salicylic acid, which, when heated with sulphuric acid, is readily resolved into phenol and carbonic acid. If small quantities are used, the reaction is more perfect even than with phenol.

It is therefore possible to prepare anthraquinon derivatives from the three isomeric oxybenzoic acids ; only in case of salicylic acid and paraoxybenzoic acid, phthalic acid must also be

present, whilst, according to Barth, oxybenzoic acid yields anthraflavon even singly.



The oxyanthraquinon obtained from phenol is no homogeneous body, but consists of two compounds, which occur in fluctuating proportions. This is at once recognised by its behaviour with baryta water and dilute ammonia. One portion dissolves readily in these liquids with a reddish-yellow colour, whilst the other forms with baryta water a deep-red lake, and is almost insoluble in ammonia. The first substance is the well-known monoxyanthraquinon; the second is a new acid compound which Baeyer and Caro name erythroxyanthraquinon.

To prepare oxyanthraquinon from the mixture of these two isomers, the crude substance is first repeatedly extracted with boiling dilute ammonia; the deep-red filtrate is mixed with hydrochloric acid, and the yellow precipitate, after washing, is several times boiled with carbonate of baryta and with water. The deep reddish-yellow filtrate, on standing protected from the air, deposits yellow needles consisting chiefly of erythroxyanthraquinon. The filtrate, when mixed with hydrochloric acid, yields a yellow gelatinous precipitate, which, when boiled, becomes more compact, and which, when recrystallised from alcohol, yields needles and leaflets of a pure sulphur yellow colour, which agree in all respects with those of oxyanthraquinon.

In order to obtain oxyanthraquinon in large quantities, it is advisable to melt the monosulphanthraquinonate of soda with two or three parts of caustic soda, and three or four

parts of water, at a low temperature. The melt soon takes a yellowish red colour, and on the addition of an acid gives a yellow or orange precipitate, consisting of oxyanthraquinon mixed with a little alizarin. If less alkali and more water be taken, a yellowish-red solution is still obtained, which on the addition of acid deposits a grass-green precipitate which dyes silk and wool direct of a green shade, and consists probably of hydroxyanthraquinon.

In order to separate the oxyanthraquinon from the accompanying alizarin, the mixture is best boiled with carbonate of lime, baryta, or lead, when soluble salts of oxyanthraquinon and insoluble alizarin salts are formed. The mixture is filtered, and oxyanthraquinon is separated from the filtrate by the aid of acids. To obtain it pure these operations are repeated several times, and the substance is then sublimed or recrystallised from alcohol. On sublimation it is obtained in beautiful lemon or orange-coloured crystals. From alcohol or ether it crystallises in fine yellow needles.

This method of separation is not, however, quite accurate, since, on the one hand, oxyanthraquinon-calcium is not very soluble in water, and alizarin-calcium is not quite insoluble. Hence on extracting the lime-salts in boiling water a certain quantity of alizarin-calcium passes into solution. Willgerodt, therefore, makes use of another method which, according to his statement, can be used as an approximate quantitative separation of the two bodies. He dissolves the mixture of alizarin and oxyanthraquinon, after the acids, salts, and anthraquinon have been removed by well-known methods, in hydrate of potassa dissolved in water and exactly calculated for the quantity employed, so that a perfectly neutral alizarate may be formed. He evaporates to dryness in the water-bath, and repeatedly extracts the finely pulverised residue with alcohol, until the solution, at first blood-red, takes a brownish-violet colour. The extracts are poured

together and evaporated to dryness, the residue again dissolved in water, when, on the addition of an acid, oxyanthraquinon separates as a straw-coloured gelatinous precipitate. The portion insoluble in alcohol is pure alizarin. The oxyanthraquinon thus obtained may be recrystallised from glacial acetic acid. It is insoluble in boiling alum-water, and sparingly soluble in boiling water.

This method presupposes an analysis of the mixture of alizarin and oxyanthraquinon, as it would be otherwise impossible to calculate the exact weight of hydrate of potassa to be employed.

Oxyanthraquinon is scarcely soluble in cold, and sparingly in boiling water; somewhat readily in alcohol and ether. With bases and carbonates it behaves like alizarin; but it has only one atom of hydrogen capable of being replaced by metals. Its salts are soluble in water with a yellowish-red colour. With concentrated sulphuric acid there is formed at low temperatures a brownish-red solution, from which oxyanthraquinon is reprecipitated unchanged on the addition of water. If the solution in sulphuric acid is heated more strongly until a precipitate no longer appears on the addition of water, a sulpho-compound is formed, not, however, identical with the ordinary sulphoxyanthraquinonic acid, but soluble in alkalis with a red-yellow colour. From boiling glacial acetic acid, oxyanthraquinon crystallises in long yellow needles. It does not dye mordanted cotton, and its melting-point is  $323^{\circ}$ .

The above-mentioned transition into alizarin is a characteristic of oxyanthraquinon. If heated with zinc powder it yields anthracen.

The baryta salt,  $[C_{14}H_7(O_2)O]_2Ba$ , separates from the hot saturated aqueous solution in yellow microscopic needles. It is not very freely soluble in water, but more readily when hot than when cold; it is insoluble in alcohol. The barytic salt of oxyanthraquinon cannot be obtained by concentration.

If we attempt to remove the excess of baryta from its solution in baryta water by means of carbonic acid, the reddish-yellow solution is completely decolourised, the salt being decomposed into carbonate of baryta and free oxyanthraquinon. The yellow precipitate which contains both substances yields, on boiling with water, a red solution of oxyanthraquinon barium, since the oxyanthraquinon with the aid of heat expels the carbonic acid of the  $\text{BaCO}_3$ . In the same manner it decomposes marble.

When a boiling concentrated solution of oxyanthraquinon in hydrate of baryta is allowed to cool, a light-red crystalline barytic salt is deposited. Oxyanthraquinon forms with cold concentrated baryta water a perfectly clear solution, but after a few minutes it separates almost completely as a red barytic salt. This compound is probably a basic salt of mon-oxyanthraquinon. If we attempt to wash it, it chiefly dissolves, and the washing water has a strongly alkaline reaction.

If mixed with alizarin, it communicates a red colour to the alkaline solution of the latter, whence it was formerly believed that alizarin contained purpurin, which has not yet been found in natural alizarin.



is obtained by heating oxyanthraquinon to  $160^\circ$  with anhydrous acetic acid. On recrystallisation from alcohol it forms small felted yellow needles. With alcoholic potassa it remains, in the cold, colourless. If heated together, the abscission of the acetyl group can be very accurately traced, as the solution very soon assumes, with increasing intensity, the reddish-yellow colour of oxyanthraquinon potassium. Ultimately pure oxyanthraquinon can be precipitated by acids.



As was mentioned in speaking of oxyanthraquinon, there



are formed by the reaction of phthalic acid and phenol two isomeric bodies—oxyanthraquinon and erythroxyanthraquinon. The latter is almost insoluble in dilute ammonia, and remains therefore undissolved on the treatment of the crude product of the action of phenol upon phthalic acid. To obtain it in a state of purity, the portion insoluble in ammonia is dissolved in hot alcohol and mixed with baryta water. The deep-red precipitate formed is washed and decomposed with hydrochloric acid, and the yellow precipitate is recrystallised from boiling alcohol. On cooling, the entire liquid is filled with yellowish-red dendritically entangled needles, which, when dry, assume a beautiful reddish-golden lustre.

The properties of the two oxyanthraquinons differ decidedly from each other in many respects, as will appear from the following tabular comparison :—

*Erythroxyanthraquinon.*

Crystallises from alcohol in agglomerated orange needles, more readily soluble in hot than in cold alcohol.

Melts at 173°–180° C.; begins to sublime at 150°; and condenses in long orange needles of the shade of sublimed alizarin. If suddenly heated in a test-tube the vapour is deposited in oily drops.

Easily soluble in dilute potash-lye with a reddish-yellow colour.

Almost insoluble in dilute ammonia; very sparingly soluble in concentrated ammonia, with a reddish colour.

Yields with baryta and lime-water a deep-red lake; almost insoluble in water, decomposable by carbonic acid, and does not decompose carbonate of baryta on boiling in water.

Forms no coloured compound with alumina.

Soluble in alcohol and ether with a yellow, and in concentrated sulphuric acid with an orange colour.

*Oxyanthraquinon.*

Crystallises from alcohol in single needles or leaflets of a pure sulphur yellow; not much more readily soluble in hot than in cold alcohol.

Melts at 268°–271° (according to Willgerodt, 323°), and sublimes at a higher heat in yellow leaflets, as also, if suddenly heated, in a test-tube.

The same.

Easily soluble in ammonia with a reddish-yellow colour.

Readily soluble with a reddish-yellow colour in baryta and lime-water; dissolves carbonate of baryta if boiled in water.

The same.

The same.

The absorption spectrum of the alkaline solution offers nothing remarkable; but there is a band in the sulphuric solution.

No band in the absorption spectrum of either the alkaline or the sulphuric solution.

Professor Kundt has compared the optical properties of the two compounds, and gives the following report on the behaviour of their solutions in concentrated sulphuric acid :—

Steinheil's Spectrum Apparatus; soda line at  $172^{\circ}$ .

*Erythroxyanthraquinon.*

(Medium Concentration.)

The blue part of the spectrum quite absorbed. Boundary of the absorption somewhat sharp at  $192^{\circ}$ ; then a dim but distinct absorption band in the green at  $185^{\circ}$ .

(Very weak Concentration.)

Blue not entirely absorbed; the maximum absorption about  $120^{\circ}$ .

*Oxyanthraquinon.*

(Medium Concentration.)

Blue part of the spectrum quite absorbed. Boundary of the absorption at  $180^{\circ}$  not so sharply defined. No band can be seen.

(Very weak Concentration.)

The extreme blue part of the spectrum not absorbed; maximum absorption about  $120^{\circ}$ .

Erythroxyanthraquinon is therefore readily distinguished from oxyanthraquinon, which it otherwise much resembles, by the presence of an absorption band in its solution in sulphuric acid.

Erythroxyanthraquinon, by the formation of baryta and lime salts, approximates much more closely to alizarin than does oxyanthraquinon. The position of the hydroxyls, however, in both corresponds to the position of each hydroxyl in alizarin. On melting with alkali, erythroxyanthraquinon yields alizarin, but it fuses less easily. The resulting alizarins are identical in their optical behaviour.

*Sulphoxyanthraquinonic Acid*,  $C_{14}H_6(O_2)(OH)(SO_3H)$ .

The formation of this acid was mentioned when treating of bisulphanthraquinonic acid. To obtain it we proceed as follows :—Bisulphanthraquinonic acid is heated till the blue

colour begins to pass into violet, some alizarin being therefore already formed. It is then dissolved in water, supersaturated with hydrochloric acid, and the filtrate is precipitated with barium chloride. If the solution is strongly acid and not too dilute, a yellow barytic salt is at once deposited; if this solution does not appear, the solution must be concentrated by evaporation. The salt thus obtained is repeatedly recrystallised from water. In this manner it is only obtained pure when the melt no longer contains any decided amount of bisulphanthraquinonic acid, from which it is not readily separable. From the baryta salt the acid is liberated by sulphuric acid, and obtained by concentrating the solution in yellow crystals very readily soluble in water and alcohol, but not in ether.

Oxyanthraquinonic acid forms two series of acids. If dissolved in hydrate of potassa, both the hydrogen atom of the sulphuric acid residue and that of the hydroxyl is replaced by potassium, and there is formed the neutral salt,  $C_{14}H_6(O_2)\overset{OK}{SO_3}K$ , soluble in water with a blue colour. If hydrochloric acid is added, the solution becomes a yellowish red, and the acid salt  $C_{14}H_6(O_2)\overset{OH}{SO_3}K$  is formed. In presence of an excess of hydrochloric acid the solution takes a yellow colour.

If the solution of the free acid, or that of the potash salt acidulated with hydrochloric acid, be mixed with barium chloride, we obtain the above-mentioned acid barytic salt,  $[C_{14}H_6(O_2)(OH)SO_3]_2Ba$ . It dissolves easily in boiling water, less readily in cold, and still more sparingly in dilute hydrochloric acid. The aqueous solution is orange, but turns yellow on the addition of hydrochloric acid. If to the aqueous solution of the salt baryta water is added, a blue compound is deposited, insoluble in water, and consisting of the neutral barytic salt,  $C_{14}H_6(O_2)\overset{O}{SO_3}Ba$ .

Hydrochloric acid withdraws the half of the barium from this salt, and the acid salt already described is formed.

The lime salt is similar to the baryta salt. If the aqueous solution of the sulphoxyanthraquinonic acid is mixed with chloride of calcium, there is formed a yellow precipitate which dissolves very readily in hot water, and is the acid salt  $[C_{14}H_6(O_2)(OH)SO_3]_2Ca$ . On slowly cooling it is deposited from the hot solution in microscopic crystals. If the aqueous solution of the acid is mixed with hydrate of lime, there is formed the neutral lime salt,  $C_{14}H_6(O_2)\overset{O}{SO_3}\}Ca$ .

With sulphate of magnesia, sulphoxyanthraquinonic acid forms an orange flocculent precipitate, which becomes violet blue on the addition of magnesia.

With acetate of lead the acid yields a violet precipitate, which turns yellow on addition of acetic acid and dissolves sparingly in water.

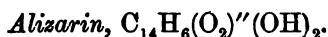
With ferric chloride there is formed a black-brown precipitate, probably  $[C_{14}H_6O_2\overset{O}{SO_3}]_3Fe$ , which turns yellow on the addition of hydrochloric acid, and may then be the acid salt of iron,  $[C_{14}H_6(OH)O_2SO_3]_2Fe$ . The latter dissolves in water with a greenish-brown colour.

Silver nitrate gives a precipitate easily soluble in hot water. If the solution is mixed with recently precipitated silver oxide, the original yellow precipitate becomes reddish violet. If the liquid in which this latter precipitate is suspended is then heated to a boil, the liquid becomes a deep brown; the silver oxide is reduced and deposited as a metallic mirror upon the sides of the vessel.

If sulphoxyanthraquinonic acid is boiled with concentrated nitric acid, it dissolves, and red vapours escape. If the solution is then evaporated in the water, fine yellow foliaceous crystals are deposited. These are easily soluble in water and alcohol; deflagrate, if heated upon platinum

foil, with great violence, and dye wool and silk a pure yellow without the greenish tone of picric acid. If the dyed tissue is heated with soap-lye the yellow colour disappears, but returns on immersion in acidulated water. The composition of this compound has not been ascertained, but we may infer from its highly explosive nature that it does not contain the sulphuric acid residue.

Sulphoxyanthraquinonic acid yields isopurpurin (flavopurpurin?) on fusion with hydrate of potassa.



The earliest chemical researches on the madder root are due to Watt, Buchholz, Hausmann, Kuhlmann, &c. These investigations related to the properties of the aqueous extract used in dyeing, its behaviour with mordants, and the formation of lakes, and did not lead to the isolation of the colouring matter and its preparation in a state of purity. This was first effected in 1826 by Colin and Robiquet. These chemists obtained both alizarin and purpurin, the former in a state of purity. The name alizarin was taken from *alizari*, the commercial term for madder roots imported from the Levant. From that time this colouring matter, which was named 'matière colorante rouge' by Gaultier de Claubry and Persoz, 'madder red' by Runge, and 'lizaric acid' by Debus, has been the subject of many and important investigations. Independently of technological experiments, there were two main problems which chemists attempted to solve. The first was the determination of the formula and composition of alizarin, and the second was the question as to whether it existed as such in the root or not.

As to the former point, it has given rise to a lengthy series of dissertations, and has only received a definite answer quite recently. It may at the first glance appear strange that the percentage composition of a body consumed every year in large quantities should not be known with

certainty. It becomes, however, quite intelligible if we reflect in what state alizarin was offered for sale. Even the best samples a few years ago contained only a small percentage of the colouring matter, and the separation of alizarin from its constant companion, purpurin, was attended with great difficulties. Pure alizarin, notwithstanding its enormous consumption, remained a chemical curiosity.

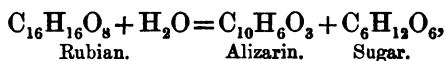
Robiquet was the first who analysed alizarin and obtained numbers which agree with the formula  $C_{14}H_8O_2$ , as now received if calculated on the correct atomic weight of carbon. Since, however, the equivalent of carbon was at that time assumed too high, he arrived at the formula  $C_{37}H_{24}O_{10}$  ( $C=6$  and  $O=8$ ). Schiel in 1846 gave the formula of alizarin as  $C_{28}H_9O_4$ , and Debus in 1848 made it  $C_{30}H_{10}O_9$ . Schunck, who at the same time analysed both alizarin itself and some of its metallic compounds, adopted the formula  $C_{14}H_5O_4$ , although his results agree better with  $C_{14}H_4O_4$  ( $C=6$  and  $O=8$ ). He observed at the same time that there is formed by the oxidation of alizarin an acid which he named alizaric acid, and to which he ascribed the formula  $C_{14}H_5O_7$ . Shortly afterwards, in 1849, Gerhardt drew attention to the similarity between alizaric and phthalic acid,  $C_8H_6O_4$ , and pronounced the two identical, on the ground of certain qualitative experiments. This view was afterwards confirmed by the analyses and comparisons of Wolff and Strecker. They thus arrived at the conclusion that alizarin and chloroxynaphthalic acid,  $C_{10}H_5ClO_3$ , which likewise yields phthalic acid on oxidation, are closely related, and they pointed out the great similarity of the two in their physical properties. In consequence of this view they assigned to alizarin the formula  $C_{10}H_6O_3$ , with which a part of the analyses of Debus and Schunck agree tolerably, and they considered chloroxynaphthalic acid as monochloralizarin. This formula of Wolff and Strecker met with very general acceptance, although Schunck subsequently came forward in defence of his own formula.

Latterly, Schützenberger and Paraf, relying upon their examination of a compound of ammonia and alizarin, proposed to double the formula, and assume it as  $C_{20}H_{12}O_6$ . In favour of this assumption Schützenberger brought forward the ethyl, methyl, and acetyl derivatives. Bally and Rosa proposed the formula  $C_{20}H_{13}O_6$ , which, however, must be at once rejected on account of the uneven number of the atoms of hydrogen. The first who arrived at the correct formula for alizarin on the basis of closely agreeing analyses was Strecker. He proposed the formula  $C_{14}H_8O_4$ , and this was confirmed by the reduction of alizarin to anthracen, effected by Graebe and Liebermann. The latter chemists did not admit the duplication of the hydrogen of Schunck's formula, because they assumed the fundamental position that alizarin contains two atoms of oxygen in the form of the group  $O_2''$ , so characteristic of the quinons, and, therefore, two atoms of hydrogen less than anthraquinon. The analyses of sublimed alizarin further agreed well with the formula  $C_{14}H_8O_4$ , whilst they all contained too little hydrogen for Schunck's formula.

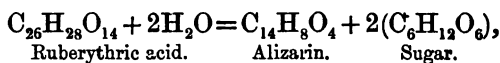
Supported by the resemblance between alizarin on the one hand and chloranilic acid,  $C_6Cl_2H \begin{pmatrix} O_2 \\ OH \end{pmatrix}''$  and chloroxynaphthalinic acid,  $C_{10}H_4Cl \begin{pmatrix} O_2 \\ OH \end{pmatrix}$ , on the other, and by the proof which they had furnished, that the two latter compounds are to be regarded as quinon derivatives, Graebe and Liebermann were led to the view that alizarin must be regarded as bioxyanthraquinon,  $C_{14}H_6 \begin{pmatrix} O_2 \\ OH \end{pmatrix}_2$ . The artificial preparation of alizarin by the introduction of two hydroxyls into anthraquinon, effected by these chemists, has confirmed the accuracy of their hypothesis.

As to the second question above mentioned, Zenneck, in 1828, was the first who conjectured that alizarin was present in madder in combination with sugar, or some other sub-

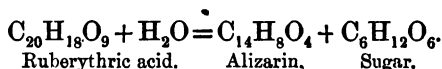
stance. In 1837, Decaisne was led by his microscopic researches to the view that alizarin was not present as such in recent madder-root, but was gradually formed on exposure to the air from a more soluble substance, and, as he assumed, by oxidation. In 1847, Schunck isolated from madder-root a compound which he named rubian, and which is resolved by acids into sugar and alizarin. At the same time, Higgins also conjectured that the formation of alizarin in extracts of madder was occasioned by a ferment. The glucoside of alizarin was first obtained in a state of purity by Rochleder, and named ruberythric acid. It is, as appears from the description and analysis, identical with the compound subsequently described by Schunck as rubianic acid. Rochleder at first proposed for his rubianic acid the formula  $C_{36}H_{40}O_{20}$  ( $C=6$  and  $O=8$ ), and subsequently  $C_{36}H_{62}O_{31}$ , or  $C_{27}H_{30}O_{15}$ . Schunck, on the other hand, gave to rubianic acid the formula  $C_{52}H_{48}O_{27}$ . Gerhardt proposed for the glucoside of alizarin the formula  $C_{16}H_{16}O_8 + aq.$ , and for alizarin, as above stated,  $C_{10}H_6O_3$ . He based this formula upon the following equation :



Now since the formula of alizarin has been definitely fixed at  $C_{14}H_8O_4$ , Graebe and Liebermann propose for ruberythric acid the formula  $C_{26}H_{28}O_{14}$ , and explain the formation of alizarin and sugar by the following equation :

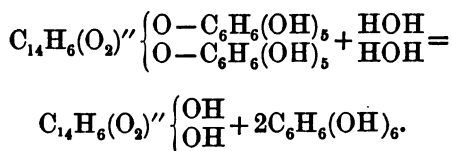


According to Gerhardt, however, only one equivalent of sugar is formed ; whence the formula of ruberythric acid would be  $C_{20}H_{18}O_9$ , and the formation of alizarin would be in accordance with the following equation :





Graebe and Liebermann's formula, however, is much more probable, as it refers this acid to the class of the quinons, and gives explanation of the transformation of alizarin and sugar. If the formula is therefore taken as  $C_{26}H_{28}O_{14}$ , we have the equation :



The analyses of Rochleder and Schunck agree with this latter formula as completely as can be expected in case of a compound so difficult to obtain in a state of purity.

|            |   | Calculated |        | Rochleder | Schunck,<br>average |
|------------|---|------------|--------|-----------|---------------------|
| $C_{26}$ . | . | 312        | 55.82  | 54.54     | 54.83               |
| $H_{28}$ . | . | 28         | 4.98   | 5.16      | 5.55                |
| $O_{14}$ . | . | 224        | 39.70  | —         | —                   |
|            |   | <hr/>      |        |           |                     |
|            |   | 564        | 100.00 |           |                     |

In 1860, E. Kopp made an important discovery concerning this glucoside; he observed, namely, that it is more permanent as regards sulphurous acid than the glucoside of purpurin. The latter, when heated with sulphurous acid, is decomposed at 50–60° C. into purpurin and sugar, whilst ruberythric acid is not split up into alizarin and sugar below 100° C. Upon this difference in behaviour Kopp founded his process for the separation of purpurin and alizarin.

The constitution of alizarin has been already considered, and we have seen that it is to be regarded as a quinonic acid, bioxyanthraquinon. This assumption is supported by its physical properties, its behaviour with reducing agents, which convert it into a compound containing two more atoms, its reduction by zinc powder, the possibility of re-

placing two atoms of hydrogen by metals and radicals, and, above all, by its formation from anthraquinon.

The madder-plant, which was till the last few years the only source of alizarin, has been known in the Levant from the earliest days, and was introduced from there through Greece and Italy into the South of France, and then into Alsace, Holland, and Germany. In Holland it has been cultivated for more than three hundred years, and it is said to have been introduced into Silesia by Hüller in 1507. In France it has been chiefly cultivated since 1756, when Jean Althen, an Armenian, settled at Avignon, and introduced its cultivation there. Avignon has remained the centre of the trade, and furnishes about one-half the entire growth of madder, whilst all other places make up the remaining half.

A tabular view of the madder exported from Avignon in the years 1860-1870 will show the importance of this article of trade.

The cultivation has suffered considerably in the last few years, in consequence of the introduction of artificial alizarin.

|                    |            |        |   |                                      |
|--------------------|------------|--------|---|--------------------------------------|
| 1860-1861 . . .    | 26,000,000 | kilos. | } | Yearly average,<br>22,815,000 kilos. |
| 1861-1862 . . .    | 27,000,000 | „      |   |                                      |
| 1862-1863 . . .    | 27,400,000 | „      |   |                                      |
| 1863-1864 . . .    | 26 000,000 | „      |   |                                      |
| 1864-1865 . . .    | 24,000,000 | „      |   |                                      |
| 1865-1866 . . .    | 26,500,000 | „      |   |                                      |
| 1866-1867 . . .    | 18,000,000 | „      |   |                                      |
| 1867-1868 . . .    | 19,500,000 | „      |   |                                      |
| 1868-1869 . . .    | 17,750,000 | „      |   |                                      |
| 1869-1870 . . .    | 16,000,000 | „      |   |                                      |
| 228,150,000 kilos. |            |        | } | Average price,<br>50 kilos., 41 frs. |
|                    |            |        |   |                                      |

Madder belongs to the natural family of the *Rubiaceæ*, to which it has given the name. Fifty-three species are recognised, of which three only have been put to industrial uses and have been accurately investigated. These are *Rubia tinctorum* in Southern, Western, and Central Europe; *R. peregrina* in the Levant; and *R. mungista* (munjeet) in India (Nepaul, Bengal), and in Japan.

Madder is a perennial plant with a quadrangular stem, small leaves, small greenish flowers, and strong, abundant roots, containing the colouring matter, which is almost absent in other parts of the plant. It succeeds best in a light sandy soil. The old roots are richer in colour than the young ones. The plant is generally allowed to grow for three years in Europe. In the Levant it is left in the ground for six years. The herb, whether fresh or dry, is a good cattle-food, and is cut for this purpose in the second year at the time of flowering.

The fresh root is from a foot to two feet long and about the thickness of the little finger; the nucleus is yellow, but the outer layer inclines more to red. After gathering, the roots are washed and dried, which is best effected in artificially heated drying-chambers, since a prolongation of the process in the open air easily produces putrefaction. When dry, they are freed by beating from the skin which adheres loosely, then ground and sent to market as powder. The principal kinds are the Dutch, the Alsatian, the Provençal or Avignon, and the Silesian.

As regards the predominating mineral constituents, the madders of commerce may be divided into calcareous (Provençal), and siliceous (Alsatian and Dutch). The ash of dried Avignon madder was determined by Bouvier as 12.6 per cent., by Schützenberger as 13.6. Chevreul found 9.8 in dried alizari, and in dried Alsatian madder 9.5–12–13.5 per cent. Very remarkable is Bouvier's statement, that half the ash consists of soluble soda-salts, and principally (5.98 per cent.) of carbonate of soda. More probable is the observation of Schützenberger, who found only 3 per cent. of soluble salts, principally chloride of potassium and a little carbonate of potassa. In Avignon madder there is a not inconsiderable quantity of lime, much of which is present as carbonate.

As above remarked, alizarin is not present in madder as such, but is formed by the splitting up of a glucoside of ruberythric acid.

The first decisive data bearing upon this supposition were brought forward by Higgin. On steeping madder in water at an ordinary temperature, he obtained a yellow liquid of a sweetish-bitter taste, which after standing for some hours lost its bitterness, deposited reddish-brown flocks, and became gelatinous. The liquid thus obtained dyed cotton reddish without any yellow tone, whilst the recent extract gave a yellow shade. He ascribed this phenomenon to the action of a ferment present in the madder-root upon a body which Kuhlmann had discovered in madder, and had named xanthin, and which is possibly the same as Runge's madder-yellow.

Xanthin, however, has not been accurately enough examined by any of the chemists, who have recognised it as an immediate principle of madder, in order to decide on its identity with madder-yellow.

According to Kuhlmann, xanthin is prepared by extracting madder with boiling alcohol, evaporation to dryness, resolution in cold water, precipitation of certain impurities with acetate of lead, filtration, addition of baryta water, collection of the barytic xanthate upon a filter, decomposition with sulphuric acid, removal of the excess of acid by baryta water, evaporation to dryness, and solution in alcohol.

According to Higgin, the madder is extracted with boiling water, certain substances not soluble in acid liquids are precipitated by sulphuric acid, the filtrate is neutralised with carbonate of soda, and digested at  $55^{\circ}$  C. with freshly precipitated hydrate of alumina in order to remove certain colouring matters; the solution is again filtered, mixed with baryta water to remove sulphuric and phosphoric acids, and the xanthin is then precipitated with solution of sugar of lead. The washed precipitate is decomposed with sulphuretted hydrogen, certain adhering substances are removed from the lead sulphide with cold water, the xanthin is then extracted with hot water, evaporated to dryness, and then redissolved in alcohol.

According to Kuhlmann, xanthin is a bright orange yellow and dyes mordanted cotton an orange shade; according to Higgin, it is a deep but pure yellow and does not dye. The former chemist ascribes to it a sweetish bitter, and the latter a pure bitter taste. It is soluble in alcohol and water, but insoluble in ether. It is decomposed on boiling with dilute hydrochloric or sulphuric acid, whilst a greenish insoluble body is separated.

From that part of the aqueous extract of madder which is not precipitated by acids, Schunck also obtained a body which he considered identical with Kuhlmann's xanthin, but as impure.

Whilst Higgin regards his xanthin as the substance from which the colouring matters are formed, Schunck found that its recent and boiling solution dyed mordanted tissues yellow, but after prolonged exposure to air and light a deep brown. Hence it is totally injurious in madder dyeing. Schunck considers, therefore, that Higgin's xanthin is not a pure substance, but a mixture consisting of a body for which he retains the name xanthin, but which, to prevent confusion, is better named chlorogenin, and of a new compound which he calls rubian.

For obtaining the latter in a state of purity Schunck proceeds as follows:—A certain quantity of madder is extracted upon a strainer by treatment with about eight parts of hot water; to the dark yellowish-brown liquid, while still hot, animal charcoal is added to the extent of  $\frac{1}{16}$ th the weight of the madder. If more charcoal is used, the rubian is not easily extracted by alcohol. It is well stirred; the animal charcoal is allowed to settle; the brown liquid is run off, and the charcoal is washed upon a strainer or filter with cold water until the washings or admixture with hydrochloric acid on boiling no longer take a green colour. The charcoal is then treated with boiling alcohol, filtered at a boil, and the process repeated till the residue

no longer colours alcohol yellow. The rubian obtained on the evaporation of the alcohol is not yet pure, since it forms a green powder on boiling with hydrochloric or sulphuric acid, and consequently still contains chlorogenin. But if again treated with the animal charcoal already used, it is obtained free from chlorogenin, or at most it requires a third treatment with the same portion of animal charcoal. Freshly ignited animal charcoal, brought in contact with a mixture of rubian and chlorogenin, takes up both these bodies; but if it has been already used it merely absorbs the former, or it gives up merely rubian to alcohol. When a portion of the alcohol with which the bone-black has been treated no longer turns green when boiled with acids, but remains a pure yellow, the alcohol is removed by distillation or evaporation. Hereby there is formed a small quantity of a dark brown flocculent matter, which is removed by filtration. The liquid then, besides rubian, contains only a small amount of another substance—a product of decomposition, possibly produced by too strong heating, and which is removed as follows. Acetate of lead is first added to the solution; the brown-red flocculent deposit is removed by filtration; from the filtrate rubian is precipitated by basic acetate of lead; the plumbic compound is washed with alcohol, and decomposed with sulphuric acid or sulphuretted hydrogen. Or the solution is freed by evaporation from a great part of its alcohol, allowed to cool, and mixed with a little sulphuric acid, when the impurities separate in brown resinous drops, which are easily removed. The sulphuric acid is then saturated with carbonate of baryta, filtered, and the filtrate concentrated in the water-bath.

Rubian forms a hard, dry brittle, shining, perfectly amorphous mass, resembling dried varnish or gum. It does not deliquesce in moist air. In thin layers it is transparent and dark yellow, but in thicker masses it appears dark brown. It dissolves readily in water, less freely in alcohol,

and not at all in ether, which last precipitates it from its alcoholic solution in brown drops. The solutions are intensely bitter. The watery solution of pure rubian is not precipitated by acids, organic or inorganic, nor by the salts of the alkalis, alkaline earths, or heavy materials in general. Impure rubian, however, yields precipitates. The only metallic compound of pure rubian is that with basic acetate of lead.

The action of nitric acid produces phthalic acid. Soda converts the yellow colour into a blue-red, but the yellow colour is restored on neutralisation.

Rubian yields much ash, to the extent of 5.2-7.69 per cent.

The most interesting behaviour of rubian is with sulphuric and hydrochloric acids. These acids have the same effect, but the products are more readily examined in case of sulphuric acid, which is more easily removed. If a considerable quantity of acid is added to an aqueous solution of rubian and heated to a boil, the liquid becomes slightly opalescent; and if a concentrated solution has been used, orange-coloured flocks soon appear. These separate on cooling in a larger quantity, and the liquid has a much paler colour.

The flocks are washed with cold water, and contain then four distinct compounds—alizarin, rubiretin, verantin, and rubianin.

To isolate these four substances Schunck proceeds as follows:—The flocks are treated with boiling alcohol, with which they form an orange solution. This is filtered at a boil, and the residue treated with more alcohol in the same way until the solvent no longer takes a deep yellow colour. Rubianin, then, chiefly remains as a yellow or brownish-yellow crystalline mass, which, after repeated treatment with alcohol, dissolves therein, and from which, as well as from the first alcoholic extracts, it separates on cooling in

yellow or brownish-yellow crystals. If the rubianin so obtained is not a pure yellow, or is imperfectly crystallised, it contains verantin, from which it is separated as follows. The deposit formed on the cooling of the alcoholic extracts is again dissolved in boiling alcohol, and acetate of lead is added, which precipitates verantin, whilst rubianin remains in solution; and as the liquid—which is filtered hot—cools, it is deposited in long lemon-yellow silky needles, which are purified by recrystallisation. The compound of verantin with oxide of lead is decomposed with sulphuric acid, and the verantin is extracted with alcohol.

The liquid from which the rubianin has separated still contains a small portion of it along with the other compounds. On adding acetate of alumina, all the alizarin, together with a part of the verantin, is precipitated as a dark red powder. The precipitate is washed with alcohol till this remains colourless, and is then decomposed with hydrochloric acid, when alizarin and verantin remain undissolved as red flocks. These flocks are washed with water, and again dissolved in alcohol, and acetate of copper is added to the solution, when verantin is thrown down in combination with oxide of copper as a reddish-brown powder. From the filtrate alizarin is precipitated by the addition of hydrochloric acid, washed with water, dissolved in alcohol, and recrystallised.

The alcoholic solution from which alizarin and verantin were jointly thrown down with acetate of alumina is evaporated to dryness, the residue mixed with hydrochloric acid, and washed with water for the removal of all acid and alumina. The residue is treated with boiling water, when brown resinous drops are precipitated, and brownish-yellow flocks float in the liquid, and are decanted from the resinous matter along with the solution. This procedure is repeated with fresh quantities of water until no more flocks are formed. The resinous mass contains chiefly rubiretin, which



is purified by solution in cold alcohol. The brownish-yellow flocks contain principally verantin and rubianin. On treatment with boiling water, rubianin dissolves, and separates in orange flocks as the solution cools; the treatment with water is repeated until nothing further is taken up.

The orange flocks of rubianin are dissolved in boiling alcohol, from which it is deposited on cooling in yellow flocks. The mother-liquors still retain a little ruberitin and alizarin, which are removed as above with acetate of alumina.

The verantin which remains undissolved on treatment with water, together with that obtained from the above-mentioned compound of the oxides of lead and copper, is dissolved in a little boiling alcohol, from which it separates on cooling as a dark-red brown or yellow-brown powder, which is purified by being re-dissolved in alcohol.

Verantin, as prepared by the above-mentioned method, is a reddish-brown powder like snuff or ground coffee. If heated upon platinum foil, it melts and burns without residue. It dissolves in sulphuric acid with a brown colour; it is almost insoluble in boiling water, but readily soluble in boiling alcohol. It is decomposed if heated with concentrated alcohol. If perfectly free from alizarin it does not dye mordanted tissues. Schunck considered purpurin as a mixture of alizarin and verantin.

Rubiretin forms a brown, opaque, resinous mass, brittle in the cold, but soft in boiling water. If heated more strongly it melts without decomposition. In sulphuric acid it dissolves with a yellowish-brown colour, and is decomposed if heated. In alkalis it dissolves with a reddish-brown colour, and is reprecipitated by acids in brown flocks. It does not dye if free from alizarin.

Rubianin forms lemon-yellow silky needles, more soluble in hot water, but less in boiling alcohol, than are rubiretin and verantin. In concentrated sulphuric acid it dissolves

with a yellow colour. In cold solutions of carbonates of soda, potash, and ammonia, it is insoluble, but in hot alkaline carbonates it dissolves with a blood-red colour. The alcoholic solution is not precipitated by neutral acetate of lead. In solution of ferric chloride it dissolves with a deep brown colour.

Schunck has also obtained a number of bodies by the action of ferments upon rubian, such as rubianin, rubiacic acid, rubiadin, rubiadipin, rubiafin, and rubiagin, and which closely resemble the substances described above.

As already stated, Rochleder was the first who obtained the glucoside of alizarin in a state of purity, and named it ruberythric acid. For the separation of this glucoside he took the following method. Oriental madder, cut in pieces, was put in boiling water, and the orange liquid thus obtained was separated from the roots. In this liquid sugar of lead produces a violet precipitation containing alizarin, purpurin, fat, sulphuric and phosphoric acids, and small quantities of other bodies. The solution is yellowish or yellowish-brown, according as it is more or less completely freed from the precipitate, and it yields with basic sugar of lead a flesh-coloured, or almost brick-red precipitate, consisting chiefly of ruberythric acid, combined with oxide of lead, and along with this another characteristic substance of an acid reaction, which Rochleder named rubichloric acid.

The latter precipitate is diffused in water, decomposed by means of sulphuretted hydrogen, and the sulphuret of lead is collected on a filter and washed. The filtrate contains phosphoric acid, citric acid, and rubichloric acid, but very little ruberythric acid. This latter compound is retained by the sulphuret of lead, from which it is extracted by means of boiling alcohol. The solution is evaporated to one-third its bulk, mixed with water, and a little hydrate of baryta is added, which produces a whitish precipitate, and is removed by filtration. The solution, when mixed with more hydrate

of baryta, yields cherry-red flocks, which are collected and dissolved in acetic acid, forming a yellow solution, whilst a little brownish-yellow matter remains undissolved. The solution is first mixed with some ammonia, but so that there is still an excess of free acid, and tribasic acetate of lead is added.

A vermilion-red precipitate is produced, which is washed with very dilute alcohol. The precipitate is then finely divided in alcohol, decomposed with sulphuretted hydrogen, and the liquid and precipitate are heated to a boil, and filtered whilst hot. On cooling and evaporation, light yellow crystals separate from the gold-coloured solution. These are purified by pressure and recrystallisation from a little boiling water. They are ruberythric acid,  $C_{26}H_{28}O_{14}$ . They form yellow prisms of a silky lustre, dissolve sparingly in cold, but readily in hot water, as also in alcohol and ether, with a golden yellow colour, but in alkalis with a dark yellow.

The aqueous solution is precipitated in dark cherry-red flocks of baryta water, and vermilion-red of basic acetate of lead. If mixed with solution of alum and ammonia a precipitate is formed, which, if dried at  $100^{\circ}C$ . and pulverised, forms a fiery red lake, resembling vermilion.

If heated to boiling with solution of ferric chloride, ruberythric acid dissolves with a deep brown colour; hydrochloric acid precipitates it from this solution in yellow flocks. If the blood-red solution of ruberythric acid in caustic alkalis is heated, the colour suddenly changes, and appears purple by transmitted, and violet blue by reflected light. It has been converted into alizarin, which is precipitated by acids in yellow flocks. The aqueous solution undergoes the same change when mixed with hydrochloric acid; it becomes first pale yellow, and then becomes turbid on boiling, whilst a yellow jelly is separated, which contracts into flocks of alizarin. The filtrate, neutralised with car-

bonate and hydrate of lead, filtered from the precipitate concentrated in the water-bath, treated with sulphuretted hydrogen, and finally evaporated in the steam-bath, leaves a syrupy residue, which has all the reactions and properties of a sugar.

The only at present admissible formula for ruberythric acid, which explains very simply its decomposition into alizarin and sugar, is, as already stated,  $C_{26}H_{28}O_{14}$ , with which the analyses of Schunck and Rochleder agree very well.

Madder, treated with mineral acids, contains, according to Rochleder, along with purpurin and alizarin, certain yellow crystalline substances, which probably also are present in the root as sugar compounds. Their amount is very trifling: thousands of pounds of madder are required to procure even a few ounces of the mixture of these bodies. Whether they are in any manner connected with the products which Schunck obtained from his rubian, or with the compounds which Schützenberger discovered in commercial purpurin, has not yet been ascertained, since the analyses executed show too little agreement.

The material from which Rochleder prepared these bodies dissolved in soda-lye with a blood-red colour. From this solution was deposited, on addition of hydrochloric acid, a copious precipitate of gelatinous dirty yellow flocks, which, on boiling in water, shrunk in volume and lost their gelatinous character, so far that they could be easily washed on the filter after cooling.

The solution in alkali and the precipitation had the object of rendering the substances more easily attacked if solvents.

On treatment with baryta water a great portion of the mass is dissolved, whilst a small part remains as an almost black powder. The soluble part is filtered from the insoluble, and the latter is washed with water.

The blood-red solution in baryta water is precipitated with hydrochloric acid; the yellowish precipitate, along with the liquid, is heated to a boil, in order to reduce the gelatinous character of the deposit, which is then collected on a filter and washed with water. When drained it is placed upon bibulous paper to remove the greater part of the moisture, and the precipitate, still damp, is then heated to a boil with so much acetic acid as is required for its perfect solution. When cold, the orange acetic solution congeals to a cake of small crystals, which is thrown upon a filter and washed with cold hydrous acetic acid till the washings have the colour of a saturated solution of bichromate of potassa.

This treatment removes an amorphous resinous body, very easily soluble in cold acetic acid, whilst but little of the other constituents pass into solution. The red solution, mixed with water, gave a yellow glutinous precipitate, too small in quantity to repay an attempt to separate its crystalline constituents.

The lemon-yellow mass remaining upon the filter is resolved into its various constituents by fractionated crystallisation from a boiling mixture of acetic acid and water, by a fractionated crystallisation of this fraction from hot alcohol, by partial solution in alcohol and partial precipitation of the alcoholic solution by means of water.

The four substances thus separated from each other approximate so closely in their behaviour with solvents that their separation can be effected only by means of oft-repeated and tedious operations, and in their properties they resemble each other so closely that numerous analyses merely serve as a proof of the necessity of further attempts at purification.

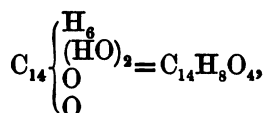
The product, most abundant in the mixture remaining after removal of the resinoid body, is named by Rochleder isalizarin, as its composition is the same as that of alizarin, from which it is readily distinguished by the blood-red colour of its solution in soda and potash lyes, and of the red

solution which it gives with baryta water. In colour, isalizarin holds a medium place between alizarin and purpurin. It does not dye cotton mordanted with iron and alumina.

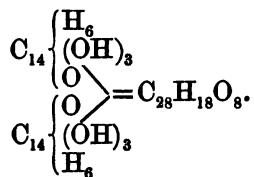
Isalizarin is accompanied by a second body, which occurs in exceedingly minute quantity in the mixture above mentioned. According to analysis, its formula is  $C_{16}H_{10}O_4$ . Its resemblance to alizarin is almost deceptive.

A third substance accompanying isalizarin, but less in quantity, is hydrisalizarin. Its colour is a lighter yellow than is that of alizarin. It dissolves in a boiling solution of ferric chloride with a dark brown colour. It is partially precipitated from this solution on cooling in the form of light yellow flocks, and partially on the addition of a few drops of hydrochloric acid, without undergoing any change. Its formula is  $C_{28}H_{18}O_8$ .

If we represent alizarin as—



then hydrisalizarin may be expressed by the following formula :



The fourth and last body which accompanies isalizarin and the two substances last mentioned is a homologue of hydrisalizarin, and has the formula  $C_{29}H_{20}O_8$ .

If exposed to a prolonged heat of  $118^\circ$ – $120^\circ$  C., this substance loses  $H_2O$ , and takes a darker colour.

Madder is now rarely used in dyeing in its original state,

except for Turkey reds. All other preparations contain alizarin either free or as a glucoside, but the foreign materials injurious in dyeing, as also purpurin, are removed to a greater or less extent. These preparations of madder are: garancin, madder flowers (*fleur de garance*), green alizarin (*alizerine verte*), extract of madder, and, since Graebe and Liebermann's discovery of the production of alizarin from anthracen, alizarin itself. These preparations, as compared with madder, have the advantage that the whole process of dyeing is simpler in execution, and that in case of topical colours the white grounds of cotton goods are less soiled than when madder is used, and can be in consequence more readily cleared.

Garancin takes its origin from the discovery of Robiquet and Colin that ground madder can be treated with concentrated sulphuric acid without injury to the colour, whilst at the same time other substances hurtful in dyeing are decomposed and removed. In 1828, Lagier, Robiquet, and Colin took out a patent for the preparation of this product, which they describe as follows:—Ground madder is stirred up with 5 to 6 parts of cold water, and left to stand over night (whereby the pigment, which was at first in solution, is precipitated along with the jelly formed from the pectin compounds), drained on a filter, and then placed under the press. The residue is treated with water in the same manner a second and a third time, and then resubmitted to pressure. The moist powder is next treated with half the weight of the original dry madder of sulphuric acid, which is diluted with more or less water as long as the mass is still hot. It is stirred until a homogeneous mixture is produced; heated to 100° C., and kept at this temperature for an hour. Lastly, it is drained upon filters, and washed till the drainings run off tasteless, then pressed, and dried on sieves.

This process is probably not carried out anywhere without modifications, but in every improved method the principle

is still the same: the action of hot dilute sulphuric acid to isolate the colouring matters which are found in madder associated with sugar, to remove the sugar and certain matters which are rendered soluble by the acid, especially to separate the pectine substances from the calcic compounds in which they exist in certain kinds of madder, to convert them into a soluble form, and to remove them by washing. The deviations from the original process are due merely to the peculiar quality of the roots to be worked up, or to subsidiary considerations.

One of the most important of these is the question whether the sugar present in the madder is to be neglected or used in the manufacture of spirits.

For the manufacture of garancin the madders of Naples, Avignon, Spain, and Holland are especially selected. The last-mentioned, as well as that of Alsace, are distinguished by their large proportion of fermentible sugar; and when the price of alcohol is high it is therefore remunerative to convert the sugar into spirit.

If this is intended, the ground madder is worked up to a homogeneous paste, with 3 to 5 times its weight of water. If too much carbonate of lime is present, 2 to  $2\frac{1}{2}$  per cent. of sulphuric acid is added to the water before bringing it in contact with the madder. The mixture is allowed to stand in tanks from twenty-four to forty-eight hours, in consequence of which the water is absorbed more completely and the paste is thickened. It is then freed from moisture by being placed in bags and submitted to hydraulic pressure. If the liquid is acid it is neutralised with ground chalk, mixed with yeast in the tank, and allowed to ferment. On the completion of the fermentation the liquid is distilled in the ordinary manner. The press-cakes are broken up, steeped again, and converted into garancin.

More frequently, however, the sugar present in the madder is neglected. But even in this case some establish-



ments begin with steeping the madder in water, pure or acidulated, and allow the mixture to stand for some days. Either the ground madder is covered with the whole quantity of water needed for the preparation of garancin, and a small percentage of sulphuric acid added, or the entire amount of sulphuric acid requisite is mixed at once with the water, and the whole allowed to stand for several days.

As a rule, the manufacturers of garancin make use of chamber acid, at most slightly concentrated in the leaden pans, but not of oil of vitriol at full strength. Of such an acid, at 40°–53° Baumé, from 15 to 25 per cent. of the weight of the madder is taken—more or less according to the quality of the root—and added to the steeping water. In many cases the preliminary steeping is omitted, and the madder is boiled at once with dilute acid. The boiling takes place in large wooden vats, holding 5,000 to 12,000 kilos. of water. These vats are conical, narrower at top, and made preferably of oak or pine-wood and bound with iron hoops, which are enclosed in strips of lead for protection against the acid. The vats are charged with water and the needful proportion of acid, and the ground madder is added, either dry or previously moistened. A leaden pipe connected with a steam boiler is passed into the vat, and forms a semicircle on the bottom, to which it is fastened. The steam should be at 2 to 4 atmospheres, and be allowed to enter freely. The mixture must be a thin paste. If the ebullition is too violent the current of steam must be checked, and if the madder adheres to the vat in any part it must be stirred from time to time. The vats are provided with covers, through which pipes are passed to convey away the steam, and the ebullition is kept up from three to six hours.

In order not to consume too much time in cooling the acid liquid, this process and the filtration are commenced at once. Below and close by the boiling vats stand the filters—flat, long wooden troughs, in the bottom of which is

a stratum of laths. Over this double bottom, along the sides, and turning over the edge, a woollen cloth is stretched. The capacity of such a trough is at least three or four times that of a vat, and it is two-thirds or three-quarters filled with cold water. Into this relatively large amount of water the hot garancin paste is allowed to flow with constant stirring. The hot liquid is at once cooled down to about 30°, at which temperature it does not attack the woollen filter-cloths. The garancin powder remaining in the vats is rinsed out with water.

In the hot liquid a not inconsiderable quantity of the madder colours are dissolved. Most of these, on mixture with the water and cooling, are precipitated upon the garancin. Hereupon the cocks at the bottom of the filtering trough are opened and the water run off. When a thick layer of solid garancin has been deposited upon the cloths it serves as a filter for the supernatant liquid, which passes through clear even when run on quickly. As soon as all the garancin is solid an equal quantity of fresh water is run in, the whole well stirred, and the liquid is run off. This washing is repeated three or four times, and the last water is allowed to drain completely off, in order to make the paste more fitted for introduction into the press-bags.

The moist garancin is then put in folding cloths or bags, which are piled up on the press-table of a vertically acting hydraulic press, and exposed to a very gradually increasing pressure. When the cake is sufficiently compressed it is still left for some time in the press, in order to allow the moisture more opportunity to drain away.

Desiccation is conducted chiefly in drying-rooms, arranged similarly to those used in the manufacture of starch. A horizontal iron flue leads the products of combustion of a furnace through the spaces to be heated, giving off heat, whilst there is simultaneous provision for the escape of the moist air. It is convenient to let the warm air enter from

above and the moist air escape below. The dried garancin is spread upon hurdles supported on scaffolding. It is convenient to place the yet moist article on the lower stages of the scaffold, and as it dries move it higher, where it is thoroughly dried by the hot dry air entering from above. This removal of the hurdles to the upper dryer and hotter strata of air is very tedious, and is impracticable where the quantities are large. Tramroads have been therefore introduced in the drying-rooms, upon which are small flat waggons carrying sheet-iron plates with turned-up margins, upon which the garancin is spread out. These waggons are emptied at doors introduced on the same level as the tramways, and charged again. Occasionally such tramways are arranged in two stages, the one above the other.

The dry garancin is then crushed in a mill resembling a common coffee-mill, then ground in another mill with vertical edge-stones like an oil-mill, sifted and packed.

Garanceux is a product resembling garancin prepared from madder grounds in dye-works by treatment at first with very weak acid and then with a somewhat stronger kind.

Madder-flower (*fleur de garance*) is a product which has been known in trade since 1851, and has been extensively used. It is obtained by fermentation. The madder is stirred up with twice its weight of water, which is then run off. The liquid is allowed to ferment, and contains most of the sugar present in the madder. The moist residue is again mixed with water, and the whole is allowed to ferment. The yield of madder-flower is from 30 to 40 per cent. of the raw material. Its tinctorial power is estimated at double that of madder, and it yields a purer purple.

Green alizarin (*alizarine verte*) was first prepared by Prof. C. Kopp, and depends upon the different action of sulphurous acid upon the glucosides of alizarin and purpurin. Whilst the glucoside of the latter, if heated with sulphurous

acid to 50-60° C., is decomposed into purpurin and sugar, that of alizarin (rubérythric acid) undergoes no change till the temperature of 100°. To prepare green alizarin, madder is mixed with ten parts of aqueous sulphurous acid, to which a little hydrochloric acid is added to decompose the lime salts present. The mixture is poured into a well-covered wooden vessel and allowed to stand for twelve to twenty-four hours, with occasional stirring. The semi-fluid mass is placed upon a filter bag, the bottoms of the cask are rinsed into the bag with a little water; the whole is allowed to drain, and the bag is submitted to a gradual but powerful pressure. The liquid is placed in a wooden vessel. The pressed mass, which is easily taken out of the bag, is again treated with ten parts of sulphurous acid, and the filtrate and expressed liquid are added to the first lot. The pressed residue is lastly treated a third time in the same manner; but the liquid obtained not being sufficiently saturated to be mixed with the former, it is used for extracting madder which has been already once treated with sulphurous acid. Lest the liquids lose their sulphurous acid too readily, they are preserved in well-covered vessels.

The liquid has a bright orange colour, with a brownish cast if highly concentrated. The taste is acid, with a sweetish-bitter after-flavour like that of madder.

The odour likewise combines the pungency of sulphurous acid with the characteristic smell of madder. In closed vessels the liquid may be kept a long time without change, though occasionally a slight brown precipitate is formed. If too much hydrochloric acid has been added along with the sulphurous, after the lapse of five to eight days a semi-crystalline deposit of purpurin of a very bright vermilion colour is often observed. This deposit is very dense, and can be readily separated by decantation, filtration, and washing.

If to the sulphurous solution there be added 3–5 per cent. of sulphuric or hydrochloric acid, no change is at first perceptible. In time, however, a flocky mass separates of a more or less decided orange colour, which gradually increases in quantity. This precipitate is more readily formed if the liquid is heated to 50°–60°. This temperature must not be exceeded, as otherwise the orange liquid assumes a deeper and deeper colour, which is communicated to the precipitate, giving this a more or less brownish or greenish-black shade.

If the temperature of 60° is not exceeded, the precipitation is completed in 20–30 minutes. The flocks often coalesce, become heavy and granular, and are separated as a more or less pulverulent mass, assuming the more beautiful a colour the denser the precipitate becomes. This precipitate, collected upon a filter, is washed with a little cold water till the washings run off with a faint yellowish or reddish colour, and have no longer an acid reaction. The precipitate is purpurin, almost chemically pure.

The mother-liquor of the purpurin is of an orange-brown colour, and can be preserved at common temperatures for any length of time in closed vessels. If heated it undergoes a remarkable change. Carbonic acid is evolved, whilst a greenish-black pulverulent mass is formed in abundance, consisting of alizarin coloured by a resinous, very deep blackish-green substance—the result of the transformation of chlorogenin under the influence of acids.

The boiling must be continued for one to two hours, to ensure the complete precipitation of the alizarin.

Very probably there is formed at the same time a small quantity of ulmin or ulmic acid derived from the action of sulphuric or hydrochloric acid upon the sugar of madder.

Green alizarin is completely precipitated in the course of twenty-four to thirty-six hours; but when in a state of

very fine subdivision it often adheres to the sides of the vessel. It can be brought to the bottom by gentle shaking and knocking.

The liquid is then run off, and the green alizarin collected upon a filter after being twice or thrice washed by decantation with cold water.

The mother-liquor is still of a deep orange-brown colour; but if the boiling has been brisk enough, and has been kept up for a sufficient time, it contains no substances useful in dyeing except the small quantity of alizarin which a slightly acidulated water can hold in solution, and which is chiefly deposited in the course of a few days. This alizarin, which is thus gradually precipitated, is generally much yellower and purer than the green alizarin.

If green alizarin is treated with alcohol or wood spirit, it dissolves with a dark yellowish-brown colour. If the alcohol is distilled off, there remains yellowish-brown alizarin almost pure, which dyes easily and well.

The extracts of madder contain the madder colours in a free state, and are obtained from the root by various methods.

J. Pernod, of Avignon, proceeded as follows:—Madder, or preferably garancine, is treated with acidulated boiling water till all colouring matter is dissolved. Any acid may be employed, but the sulphuric is preferred from its cheapness. The best proportion is 5 grms. acid to 1 litre river water. The liquids obtained are collected and allowed to stand; on cooling an orange-red precipitate separates; the mother-liquor is then drawn off and used for the treatment of a fresh portion of madder. The precipitate is freed from acid by washing with river water till the washings have a rose colour. The precipitate is then drained, thickened with starch or gum, and is at once ready for use.

Another procedure laid down by A. Rien, of Avignon, is based upon the fact that water, whether pure, acidulated,

or mixed with a little alum, dissolves the madder colours at a pressure of four to five atmospheres, and re-deposits them on cooling. He proceeds as follows:—Ground madder is washed with cold water to remove sugar and pectin, and then dried. The powder is then placed in a basket of very closely woven wire, hanging on an axle which passes through a stuffing-box into a Papin's digester. The digester must be able to bear a pressure of four to five atmospheres, and the basket can be set in motion by means of the axle. The digester is entirely or partially filled with water, which is mixed with a little acid in order to free the madder from its lime. After all apertures have been carefully closed, it is heated either directly over the naked fire, or by means of steam, so that the temperature in the interior of the apparatus may correspond to a pressure of four to five atmospheres. At the set time the axle, and consequently the basket, are set in revolution to promote the extraction. After about 15–20 minutes the apparatus is emptied by a cock, before which a disc of felt is fixed as a filter, into suitable vessels in which the dissolved colour is deposited as the liquid cools. At the same time the apparatus is re-filled with water, pure or acidulated, in order to extract a still further amount of colour from the madder, which is left in the basket as long as it yields colour. It is again exposed to steam at five atmospheres for a quarter to half an hour, and the basket is allowed to revolve. The liquid is again allowed to cool, and the same treatment is repeated till the madder is exhausted. The liquids obtained by this process deposit on cooling orange-red flocks, which are collected on a filter and dried. They form a colouring matter which is neither pure alizarin nor purpurin, but is very rich and well adapted for printing. The liquid, from which the flocks have been deposited, may be used instead of plain water for filling the digester, and is found to have a greater solvent power.

Schützenberger prepared an extract of madder, having procured a cast-steel cylinder of such thickness that it could bear the pressure of thousands of atmospheres. In this cylinder, which was capable of being hermetically closed, he dissolved the alizarin in pure water at a very high pressure, and allowed it then to crystallise on cooling.

In order to prepare pure alizarin from madder, it is first washed with water and then boiled with alum. The solution is allowed to stand for several days, the precipitate collected, boiled repeatedly with dilute hydrochloric acid, washed with water, and the residue dissolved in alcohol, from which it is separated by evaporation. The colouring matter, not yet quite pure, is dissolved again in a little alcohol, boiled repeatedly in alum water till this is no longer coloured, the residue dried and dissolved in ether and sublimed.

According to Kopp's method, we obtain pure alizarin by mixing the sulphurous solutions, from which the purpurin has been deposited on gently heating, with milk of lime till the reaction is slightly alkaline. The result is a deep violet solution of alizarin-lime, which is decomposed whilst still moist with an excess of hydrochloric acid. The alizarin deposited is of a deep orange-brown colour, and settles readily. It is collected on a filter, well washed, dried, and sublimed. It is thus obtained in fine orange crystals, which are so much the redder as the sublimation was effected at a higher temperature.

As already stated, Graebe and Liebermann were the first who succeeded in obtaining alizarin artificially. They first prepared it by melting bibromanthraquinon with hydrate of potassa, and then discovered that the sulphuric acid compounds of anthraquinon might be more advantageously used. On boiling bibromanthraquinon or the sulphanthraquinonic acids with hydrate of potash, the ready transformation does not appear which is observed in the chlorinised quinons of benzol and naphthalin ; but on inspissation with concentrated



lye this reaction appears, and the mass takes a deep violet colour, a sign of the formation of alizarin.

The identity of artificial and natural alizarin was contested at first, but has been established beyond a doubt by the minute researches of Schunck, Perkin, Bolley, E. Kopp, and others.

The history of the methods of obtaining artificial alizarin shows most distinctly how the originally costly and difficult reactions have been gradually modified, and how very expensive agents have step by step been replaced by cheaper ones, whilst the quality and purity of the product has been still rising.

We must mention the patents which have been obtained for the preparation of artificial alizarin, of which the first has now merely a historical interest, whilst some of the subsequent ones are of no value for work on a commercial scale.

The first process given by Graebe and Liebermann is as follows:—

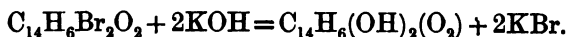
Purified anthracen ( $C_{14}H_{10}$ ) is converted into anthraquinon,  $C_{14}H_8O_2$ , as follows:—

1. By heating 1 part anthracen with 2 parts bichromate of potassa and sulphuric acid, with or without the action of glacial acetic acid.
2. By oxidising anthracen with bichromate of potassa, both dissolved in glacial acetic acid.
3. By oxidising anthracen with nitric acid moderately concentrated, with the simultaneous use of concentrated acetic acid.

Anthraquinon obtained by any of these three methods is purified and converted into bibromanthraquinon,  $C_{14}H_6Br_2O_2$ , by heating 1 mol. anthraquinon and 4 mol. bromine for some hours to  $80^{\circ}$ – $130^{\circ}$  in closed vessels.



The bibromanthraquinon is then heated for some time in closed vessels to 180°–260°, along with concentrated soda or potash-lye, in order to replace the bromine by hydroxyl.



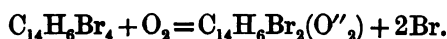
The mixture gradually turns first blue and then violet, which becomes more and more intense. When the colour no longer deepens, the mixture is allowed to cool, dissolved in water, filtered, and supersaturated with sulphuric or muriatic acid, when alizarin is deposited in yellow flocks, which are filtered off and purified by washing with water.

According to a second process likewise patented by Graebe and Liebermann, the direct formation of anthraquinon is avoided, and bibromanthraquinon is prepared at once. This is done as follows:—

Anthracen is treated with bromine in excess, and converted into bibromanthracentetrabromide,  $\text{C}_{14}\text{H}_6\text{Br}_2\text{Br}_4$ . In contact with alcoholic potash this is converted into tetrabromanthracen,  $\text{C}_{14}\text{H}_6\text{Br}_4$ .



Tetrabromanthracen, if heated with five parts of sufficiently diluted nitric acid to 100°, loses bromine and yields bibromanthraquinon.



This compound is then converted into alizarin as above described, by treatment with hydrate of potash.

Graebe and Liebermann declare at the same time that in all cases chlorine may be used instead of bromine.

In 1869 (May 28), Broenner and Gutzkow obtained an English patent, the essential parts of which are as follows:—Anthracen is converted into a new product by oxidation and

substitution. For this purpose some one of the well-known oxidising and substituting agents is employed, such as acid chromate of potassa and sulphuric acid or crystalline acetic acid, but especially nitric acid is used. The new product is purified either by crystallisation, sublimation, or in any other manner, and the colouring matters are obtained by oxidation, or, if necessary, by treatment with potash. The colouring matters may also be directly obtained from the crude product. For this purpose it is preferably dissolved in sulphuric acid, with the addition of any oxidising agent, such as nitric acid and the nitrates, sulphates, oxides and peroxides of metals, or their compounds with acids which are easily reduced, such as the arsenic, chromic, or other acids, or the metallic chlorates.

By this method Broenner and Gutzkow say they have obtained two distinct colouring matters, one of which dissolves in alcohol with a yellow, and the other with a red colour.

In their final specification, Broenner and Gutzkow recommend the following process. The anthracen is first converted into an oxidised product, which is effected by treatment with nitric acid, or bichromate of potassa and sulphuric acid or acetic acid, &c., and purification of this product by crystallisation or sublimation.

The first colouring matter, which tinges alcohol yellow, is then obtained by melting the oxidised product with alkali, or by dissolving it first in sulphuric acid or in another acid, or a mixture of acids, so as to obtain the product not crystalline, but in a flocculent condition, upon which the alkalis may act more readily. After solution in sulphuric acid, &c., the product is precipitated with water, and the resulting precipitate, as above stated, is melted with potash. If nitric acid is applied, or a mixture of nitric and sulphuric acid, or sulphuric acid and nitrates, we obtain a nitro-product which either yields a colouring matter when heated with alkali, or

is converted into another compound by the action of reducing agents, e.g. hydrochloric acid and metals. Whichever method is taken, the ultimate product is precipitated with acids, filtered, and washed with water. If a colouring matter is desired which dyes a yellowish-red with aluminous mordants, there must be added to the colour after solution in acids nitric acid or nitrates (e.g. mercurous nitrate), either at a common temperature or with the aid of heat. It appears on careful study that what is claimed in this patent is the fusion of anthraquinon with alkalis and the production of nitro- or of amidoanthraquinon.

Anthracen is first to be converted into a new product by oxidising agents, chromate of potassa, &c.; this is anthraquinon. This product is then either at once to be fused with alkalis or, in order to make it more flocculent, it is first dissolved in sulphuric acid, then precipitated with water, and the precipitate melted with alkalis. This precipitate is merely anthraquinon, but in a purer state, as on treatment with sulphuric acid the impurities are converted into soluble sulpho-compounds, and are removed from the precipitate on filtration. The fusion of this product leads to the same result as the melting of the crude matter with alkali.

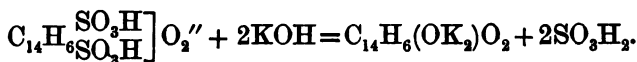
If anthracen is treated with nitric acid, with nitro-sulphuric acid, or with sulphuric acid and nitrates, the main product is dinitroanthraquinon, which, if melted with alkali under suitable conditions, yields alizarin, and on treatment with reducing agents is converted into diamidoanthraquinon, which tinges alcohol red and dyes silk and wool the same colour.

The production of sulphoanthraquinonic acids according to this specification is out of the question, as there is no mention of a solution, but of a precipitate, thrown down from the sulphuric solution by the addition of water. That this precipitate is no sulpho-compound is evident from the

fact that these compounds dissolve readily in water instead of being precipitated thereby.

Anthraquinon on fusion with potash yields mere traces of a colouring matter, which is not even proved to be alizarin at all. Further, dinitroanthraquinon is convertible into alizarin only with great difficulty; whilst diamidoanthraquinon has little tinctorial power, dyes merely flat and fugitive shades, and can be easily replaced by other brighter and cheaper colours.

About the same time Graebe, Liebermann, and Caro, and also Perkin, studied the action of sulphuric acid upon anthraquinon, and applied this principle to the manufacture of alizarin. The English patent of the three former chemists is dated 1869, June 25; that of Perkin was taken out a day later, but was sealed earlier. Perkin treats anthraquinon,  $C_{14}H_8O_2$ , with highly concentrated sulphuric acid at elevated temperatures, and thus converts it into  $C_{14}H_6 \left[ \begin{smallmatrix} SO_3H \\ SO_3H \end{smallmatrix} \right] O_2$ . On fusion with an alkali the two sulphuric residues,  $SO_3H$ , are replaced by hydroxyl and  $HO$ , and alizarin is formed.



Perkin observed on this occasion during the fusion of bisulphanthraquinonic acid the formation of an intermediate product, sulphoxyanthraquinonic acid,  $C_{14}H_6 \overset{OH}{SO_3H} (O_2)''$ , which imparts a blue colour to the alizarin melt.

In the meantime, Graebe, Liebermann, and Caro had taken a further important step in the simplification of the process. Both in their English patent and in their French patents of November 3, 1869, and January 18, 1870, they dispense with the preparation of anthraquinon. This they effected by the direct conversion of anthracen into bisulphanthracenic acid, and its transformation into bisulphanthra-

quinonic acid by means of oxidising agents. A twofold advantage was thus to be secured. In the first place, the oxidation of sulphanthracenic acid to sulphanthraquinonic acid is supposed to be simpler and more complete than the oxidation of anthracen to anthraquinon, where the formation of smeary and useless by-products is almost inevitable. Secondly, very cheap oxidising agents were to be employed.

The patents mentioned contain the following directions for the preparation of artificial alizarin :

1. By preparing bisulphanthraquinonic acid from anthraquinon.

One part of anthraquinon is mixed with about 3 parts of concentrated sulphuric acid (spec. grav. 1.848), and the mixture is heated in a vessel—not attacked by sulphuric acid—to about 260° C., until a sample poured into water dissolves completely or leaves mere traces of unconverted anthraquinon.

It is then allowed to cool and diluted with water. To remove excess of sulphuric acid it is accurately neutralised with chalk. Sulphate of lime is deposited, which is removed by filtration, and is powerfully pressed, whilst bisulphanthraquinonate of lime remains in solution. As this salt is not soluble in cold water, these operations are carried on at a boiling heat.

The hot solution of the lime salt is then mixed with a solution of carbonate of potash or soda, also hot, till the reaction becomes alkaline. The mixture is boiled for some time till the carbonate of lime is deposited in a dense, granular state. The solution of bisulphanthraquinonate of soda is decanted or filtered, and evaporated to dryness.

To 1 part of the dry salt are added 2 to 3 parts of solid potash or soda and a little water, in order to promote the fusion of the hydrate and facilitate the mixture of the salts. The mixture is then heated in iron or copper vessels to about 180°–260° for an hour, or better, till the

melt takes a deep blue violet colour, and a portion dissolved in water and mixed with sulphuric acid gives a copious brownish-yellow precipitate. When the point has been reached it is allowed to cool, the melt is dissolved in hot water, the dark violet blue solution is, if needful, decanted from the insoluble residue, or filtered through linen, and the clear liquid is mixed with sulphuric or hydrochloric acid. Sulphurous and carbonic acids are developed, and at the same time alizarin is deposited in dense large flocks of a yellowish-brown. When cold, the precipitate is collected on a filter and thoroughly washed with cold water. The alizarin thus obtained is fit for all purposes to which the preparations of madder have been hitherto applied.

## 2. *Preparation of Bisulphanthraquinonic Acid from Anthracen.*

One part of anthracen is heated in a suitable vessel with 4 parts of sulphuric acid, at first for about three hours, to 100°, when the temperature is raised to 150° or even higher for at least another hour. The cold mass is diluted with 3 parts of water. If unconverted anthracen is here deposited, it is collected, washed, dried, and added to another operation. The washing waters may be employed instead of pure water for diluting bisulphanthracenic acid.

The dark-coloured and highly acid solution contains bisulphanthracenic acid,  $C_{14}H_8SO_3H$ , and much free sulphuric acid. It is heated to a boil with the addition of three times as much powdered native manganese as the original weight of anthracen. The ebullition is kept up till the bisulphanthracenic acid is converted into bisulphanthraquinonic acid by taking up oxygen from the manganese.

Manganous sulphate is formed at the same time. It is advisable to evaporate to dryness, and continue the

heat even for some time longer to ensure complete conversion.

The mass is next dissolved in boiling water, and mixed with diluted milk of lime till the reaction becomes alkaline. The lime decomposes the salts of manganese, precipitates insoluble manganous oxide; whilst there are formed at the same time sulphate of lime, almost insoluble, and bisulphanthraquinonate of lime, which remains in solution.

All insoluble matter is removed by filtration and pressure, and a clear solution of bisulphanthraquinonate of lime is obtained, which is then decomposed by an alkaline carbonate.

The solution of the salt thus produced is evaporated to dryness, and converted into alizarin by melting with hydrate of potash, as already described.

Instead of peroxide of manganese, the peroxide of lead, chromic or nitric acid, may be used. If the oxidising agent is soluble in water, as, e.g., chromic acid, all excess must be removed before the milk of lime is added. For this purpose sulphurous acid is passed into the solution, which, after oxidation, contains sulphuric acid, chromic oxide, bisulphanthraquinonic acid, and the excess of chromic acid, until all the latter is reduced to oxide, which, as well as the sulphuric acid, is then precipitated by milk of lime.

If nitric acid is applied as an oxidising agent, the mixture of sulphuric and bisulphanthraquinonic acids, which still contains the excess of nitric acid, must be concentrated until even the sulphuric acid begins to volatilise. The mixture is then allowed to cool, and diluted with water before the milk of lime is added.

On November 17, 1869, Perkin patented another process, according to which anthracen is first converted into dichloranthracen, a dichloro-substitution-product. If this is treated with sulphuric acid, sulpho-compounds are formed which still contain chlorine. In order to convert this into sulphanthraquinonic acid, an oxidising agent is added—e.g., peroxide of



lead—and heat is applied till the solution of the sulpho-compound no longer fluoresces. In the final specification of his patent, Perkin subsequently stated that the addition of oxidising agents might be avoided if the mixture of dichlor-anthracen and sulphuric acid is heated to about  $210^{\circ}$ .

Bisulphanthraquinonic acid is thus at once obtained, which is freed from excess of sulphuric acid, and from the accompanying carbonaceous matters by boiling with milk of lime; from the bisulphanthraquinonate of lime, the soda salt is then obtained by boiling with carbonate of soda, and alizarin is then produced by melting with a caustic alkali.

On January 24, 1870, Dale and Schorlemmer patented a process which, if it had held good on the large scale, would have been a further simplification.

Their process is as follows:

One part of anthracen is boiled for some time with 4 to 10 parts of strong sulphuric acid, then diluted with water, the solution neutralised with carbonate of lime, baryta, soda, or potash, and the sulphates removed by filtration or crystallisation. The resulting solution is heated to  $180^{\circ}$  to  $260^{\circ}$  with caustic alkali, to which a quantity of nitre or chlorate of potash, equal in weight to the anthracen employed, has been added until a violet-blue colour appears. From this product alizarin is obtained by precipitation with acids.

The bisulphanthracen acid is first converted into bisulphanthraquinonic acid by the action of the saltpetre or the chlorate of potash, and the latter acid is changed into alizarin by the excess of alkaline hydrate. In this process the quantity of saltpetre or of chlorate must be very accurately adjusted, as there is always danger that the alizarin when formed may be burnt up and destroyed by the oxidising agent. On the other hand, the incomplete conversion of bisulphanthracenic acid into the bisulphanthraquinonic is a source of loss.

On September 6, 1872, Meister, Lucius, and Brüning obtained a patent based upon the preparation of binitroanthraquinon.

Purified anthracen melting between  $207^{\circ}$  and  $210^{\circ}$  is heated for about three hours in enamelled iron vessels with a fourth of its weight of potassium bichromate and 12 parts of nitric acid at 1.05 spec. gravity. The resulting crude anthraquinon is dissolved in 6 parts of boiling nitric acid, spec. gr. 1.5. The solution is known to be complete when a portion no longer deposits anthraquinon on cooling. The liquid now contains mononitroanthraquinon, which is deposited as a yellow precipitate on the addition of water. This is washed and dried and heated with 9 to 12 parts soda-lye at spec. gr. 1.3 to 1.4 to  $170^{\circ}$  to  $220^{\circ}$  in suitable vessels. The heat is withdrawn, when a sample taken out no longer shows an increased precipitate on the addition of hydrochloric acid. The mass is then cooled, dissolved in boiling water, filtered, and the colouring-matter precipitated from the hot filtrate by the addition of an acid.

The residue on the filter, consisting chiefly of anthraquinon, can be re-nitrated and again worked up. The acid mother-liquor of the mononitroanthraquinon and the acid recovered by the condensation of the vapours volatilised during the conversion of the anthracen to anthraquinon can of course be used again.

On April 16, 1874, G. Auerbach and Th. Gessert obtained a patent for alizarin and isopurpurin, according to which anthracen is heated with sulphuric acid to  $250^{\circ}$ : the sulpho-compound formed is either first purified with lime, or at once melted with alkali, and the melt treated with acid in the usual manner.

Of subsequent patents, those of Holliday and Sons and of Gauhe of Barmen are mere repetitions of earlier processes. That of Gauhe is almost an exact copy of the Gessert-Auerbach patent, with this only difference, that Gauhe calls the

sulpho-acid which he obtains by heating anthracen to 250° C. with sulphuric acid 'anthracendisulphuric acid.' Holliday converts the anthraquinon into bibrom- or bichlor-anthraquinon, and converts this into bisulphanthraquinonic acid by treatment with sulphuric acid. The colour is then obtained by the usual treatment with alkali.

Of all these methods, two only, that of Graebe, Liebermann, and Caro (oxidation of anthracen to anthraquinon and conversion into sulphoquinonic acid), and that of Perkin (dichloranthracen), are practically applicable. The former has, however, an advantage over the latter, as it yields almost exact quantitative results, whilst the dichloranthracen method involves not inconsiderable loss and many tedious operations.

The remaining methods, bromanthraquinon, &c., are impracticable on account of the high price of the raw material and the troublesome nature of the necessary apparatus; or, as in case of sulphanthracenic acid (direct oxidation of anthracen with sulphuric acid), they yield isomeric sulpho-compounds, which on further treatment with alkali yield no alizarin.

The main advantage of Graebe, Liebermann, and Caro's process as compared with that of Perkin is the possibility of obtaining at will any desired tone, from the most blue, i.e. pure alizarin, to the yellowest isopurpurin, whilst on the dichlor-method the yellow tones only are produced. These yellow alizarines, however, are distinguished from the yellow alizarin prepared from anthraquinon by the brightness of the rose and violet shades which they yield, due probably to the large amount present of flavopurpurin, which, in spite of its yellow cast, gives a beautiful violet and a bright rose.

As already stated above, alizarin is formed only from the monosulphanthraquinonate of soda, whilst the various disulpho-compounds yield trioxyanthraquinon. To prepare a

pure or blue alizarin a pure monosulphoanthraquinonic acid must be obtained. The method laid down under monosulphoanthraquinonic acid is therefore followed, and the salts are purified by repeated crystallisation or by other suitable methods. The monosulphanthraquinonate of soda finally obtained, known by manufacturers as silver-salt, is heated with 3 to 4 parts of caustic soda in aqueous solution, and melted till a specimen on mixture with acids shows no further increase in colouring-matter, and all monoxanthraquinon has been converted into alizarin.

The fusion with alkali is one of the most important steps in the whole manufacture of alizarin. The addition of water, the temperature, the duration of the melting, are of the greatest moment. If too much water is added, we obtain either hydro-products or only oxyanthraquinon, as also happens if the temperature is too low. If the heat is too great, a part of the melt burns and a dirty green paste is obtained, which dyes greyish shades. If it is heated too long or too slowly, a part of the sulpho-salt is reduced to anthraquinon, which cannot be easily separated from the alizarin, since the alkaline solution of alizarin is exceedingly difficult and tedious to filter. To avoid this reduction it has been proposed to add to the melt oxidising agents or to force in air. In melting in the so-called baking-ovens, where the melt is spread out in very thin layers, the air finds ready access to the mass, and may thus prevent reduction. If the melting is performed in these 'baking-ovens,' the mass must be previously concentrated in other vessels down to the proper consistence before it can be placed in the flat pan-like trays. This occasions double labour, and gives opportunity for loss. It is better therefore to complete the melting in a single apparatus, and for this purpose the most suitable are iron boilers with strong edges, capable of being closed air-tight, and of bearing a pressure of several atmospheres. The sulpho-salt of soda, with the necessary quantity

of caustic alkali and water, is introduced into the boiler, stirred well, and heated to  $180^{\circ}$ – $200^{\circ}$ . If a sample taken out on the addition of acid shows no increase of colouring matter, and if all oxyanthraquinon and sulphoxyanthraquinonic acid have disappeared, the operation is at an end. Sulphoxyanthraquinonic acid is determined by taking a small portion of the melt, dissolving in water, neutralising with acid, and filtering. The filtrate is shaken with ether, whereby the alizarin and isopurpurin are dissolved, whilst the sulphoxyanthraquinonic acid, being insoluble in ether, remains in the aqueous solution, and can be detected by the blue colour which it gives with potash. To detect oxyanthraquinon and anthraflavic acid, an aqueous solution of the melt is heated with caustic lime, boiled, and filtered. If the filtrate is orange, and deposits yellow flocks on the addition of an acid, those substances are still present.

As on melting under pressure a considerable amount of hydrogen is evolved, which reduces the sulphoanthraquinonic acid to anthraquinon, and even to benzoic acid, some manufacturers add chlorate of potash to the melt, which gives off oxygen at elevated temperatures, and thus renders the hydrogen harmless. Instead of the chlorate, nitrite of potash may be used. Both, however, render the tone of the colour more yellow.

When the melt is complete, it is diluted with water in suitable vessels, heated to a boil, and neutralised with sulphuric or hydrochloric acid. The alizarin is then deposited as an extremely fine powder, which is separated from the liquid by filtration, or preferably by passage through a filter press. It is then washed with water till the washings have no longer an acid reaction, and the somewhat thick mass or cake is introduced into the stirring apparatus, where it is converted into a stiff paste. By determining the amount of actual colour, and adding the necessary amount of water, it can be let down to the strength desired. The finished paste

is now sold in wooden casks. Zinc boxes were formerly employed, but must be rejected, as the alizarin gradually combines with the zinc, and requires to be liberated from the zinc-alizarate formed by the addition of an acid.

Alizarin paste is commonly sold at the strength of 10 or 15 per cent., rarely 20. To save freight, it would be better to adopt a higher standard; but practice has shown that pastes of a high percentage are not easily diluted with water to the strength required in dye-works. Dry alizarin, which is very easily prepared, cannot, when ground up in water, be reduced into the fine condition in which it is found in the paste, and if used in dyeing, it involves loss, and renders the goods spotty.

Pure alizarin can be prepared from the paste in various ways. The best method for obtaining it in a state of chemical purity is to begin with an absolutely pure monosulphanthraquinonate of soda.

To prepare it from the paste, it is dissolved in dilute soda-lye, and freed by filtration from the undissolved anthraquinon. The alkaline solution is mixed with chloride of barium, heated to a boil in order to make the precipitate dense and granular, filtered, well washed with water, suspended in water, and decomposed with an acid. The orange precipitate is filtered, washed, dried, and sublimed or recrystallised from glacial acetic acid, and consists of nearly pure alizarin.

Or a rapid current of carbonic acid is conducted into the filtered alkaline solution. The violet colour quickly changes into red, and as alizarin is but sparingly soluble in sodium bicarbonate, it is soon deposited along with the latter compound tinged red. The alizarin is often found attached to the sides of the vessel in beautiful orange crusts. The precipitate is filtered off and decomposed with an acid. The filtrate has generally but a faint red colour, and, on admixture with acid, yields a little impure alizarin. That obtained on

mixing the precipitate with an acid yields on sublimation splendid crystals.

Willgerodt employs the following method for the purification of alizarin: After the acids, salts, and the anthraquinon have been removed by known methods, he dissolves the alizarin in an aqueous solution of hydrate of potash, exactly proportionate to the quantity employed, so as to form a perfectly neutral alizarate; he evaporates to dryness in the water-bath, and extracts the finely powdered residue with alcohol till the infusions, which were blood-red at first, become a brownish-red. They are then collected together and evaporated to dryness. The residue is dissolved in water, when pure oxyanthraquinon separates as a straw-coloured gelatinous precipitate, whilst the portion of the first dry residue, which was insoluble in alcohol, consists of pure alizarin. This method, however, is only applicable when the proportion of alizarin present is known, since oxyanthraquinon has a different molecular weight, whence the amount of alkali to be employed cannot be calculated from the crude alizarin.

Grimm's reaction, the action of phthalic acid upon phenols, led Baeyer and Caro to the synthesis of alizarin from phthalic acid and pyrocatechin.

If these two compounds are brought in contact with sulphuric acid, the mass, when gently heated, turns a fine rose-colour, and yields with water a colourless liquid, which becomes of a splendid blue on treatment with potassa. Phthalein is undoubtedly first formed. If the temperature is raised to  $140^{\circ}$  C., the mixture of the three substances takes a brown colour, and after some time water precipitates a brown-black mass, which, when well washed with water, is partially soluble in alcohol. The residue obtained on evaporation of the alcohol yields on sublimation alizarin. Professor Kundt found its absorption-bands identical with those of alizarin.

For the sublimation of alizarin the best process is that of Schützenberger. The alizarin is introduced into a broad porcelain crucible, 5 to 6 centimetres in height, and covered with a piece of blotting paper and with its lid. It is then placed upon a sand-bath, and heated till the layer of sand surrounding the crucible reaches a temperature of  $250^{\circ}$ – $280^{\circ}$ . The alizarin is thus obtained in fine orange-coloured crystals, which are the redder, the higher the temperature. As residue, there remains a small quantity of a shining black carbon. If pure alizarin is sublimed in a current of carbonic acid, it sublimes entirely without residue.

Experiments on the tinctorial power of artificial alizarin compared with the natural have been repeatedly undertaken, but with very various results. Whilst some chemists assume that natural and artificial alizarin are not identical, others maintain the opposite; and the latter view is the more probable, since the artificial alizarin employed was not pure, but contained more or less of matters capable of dyeing, but not of bearing the clearing process, such as oxyanthraquinon, and sulphoxyanthraquinonic acid. Thus Christie declares that tissues dyed with artificial alizarin gave off much crimson colouring matter on treatment with soda-lye. Hoog, on the other hand, maintains that goods dyed with pure artificial alizarin stand soaping better than those dyed with garancin.

According to Bolley, the alizarin paste of Gessert and of Meister and Lucius has from 10 to 12 times the tinctorial power of the garancin made in Italy. For Turkey reds, both give very brilliant but somewhat yellowish colours, due to the presence of a certain quantity of anthrapurpurin.

Alizarin can be obtained in crystals either by sublimation or by solution in ether or alcohol and evaporation. From hydrous ether it is obtained in crystals of the formula  $C_{14}H_8O_4 + 3H_2O$ , containing 18.3 per cent. of crystalline water. These crystals form needles of a golden lustre, resembling aureum musivum. From alcohol, benzol, coal-tar



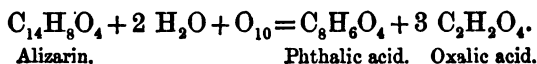
oil, petroleum, and water, it is obtained in prismatic needles. It dissolves also in hot acetic acid, which, on cooling, deposits it in yellow crystals. If heated to 100° C. it loses its crystalline water, melts at 277°, and sublimes at 215°–240°. Very often it volatilises even at 100°.

In cold water it is almost insoluble. According to Schützenberger and Mathieux Plessy, 100 grms. water dissolve—

|         |   |   |   |                      |
|---------|---|---|---|----------------------|
| At 100° | . | . | . | 0.031 grms. alizarin |
| 150°    | . | . | . | 0.035 „ „            |
| 200°    | . | . | . | 0.820 „ „            |
| 225°    | . | . | . | 1.700 „ „            |
| 250°    | . | . | . | 3.160 „ „            |

In cold alcohol also it is sparingly soluble. The boiling alcoholic solution is yellow, and on cooling deposits needles of anhydrous alizarin. In bisulphide of carbon it is sparingly soluble, but readily in hydrocarbons, and the more the higher is their boiling-point.

If the solution of alizarin in hydrocarbons is treated with caustic alkaline lyes, the alizarin is withdrawn, a reaction which Kopp has availed himself of in preparing yellow alizarin from alizarine verte. It is freely soluble in hot wood spirit, aceton, and glycerin. Hydrochloric, sulphuric, and phosphoric acids do not affect it, and dissolve it very sparingly even when heated. Sulphuric acid at 66° B. dissolves it with a reddish-brown colour. The solution can bear a heat of 150° to 200° without change, and on the addition of water alizarin is deposited in yellow flocks. Alum and sulphate of alumina dissolve it but sparingly even at the boiling-point, and on cooling almost all the alizarin is redeposited. Nitric acid attacks alizarin with the evolution of red vapours, and formation of phthalic and oxalic acids.

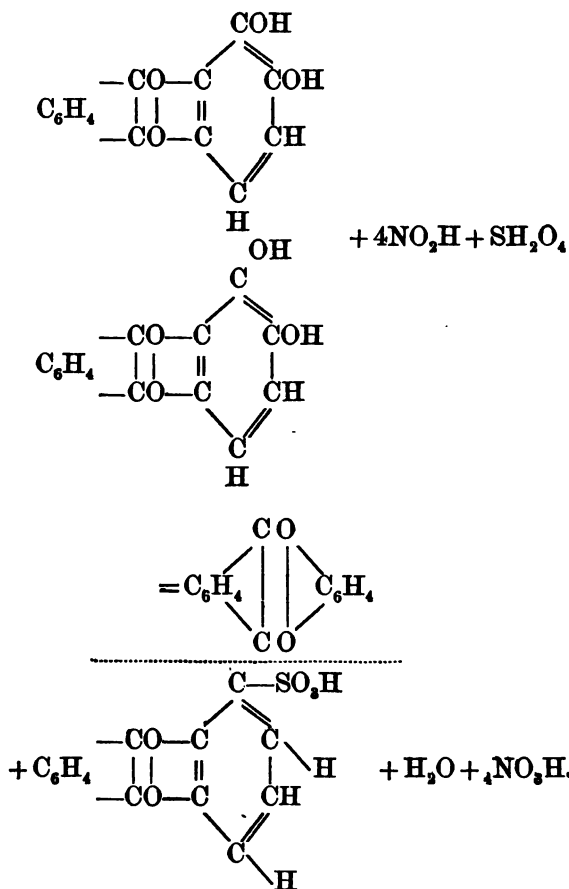


Schunck also oxidized it by boiling with ferrous salts (chloride or nitrate).

If heated with zinc powder it yields anthracen. This reduction is performed like an ultimate organic analysis. The alizarin is mixed with zinc powder and introduced into a tube the anterior portion of which is filled with a long layer of pure zinc powder. It is then gradually heated to redness, beginning at the anterior end. Anthracen is then deposited in fine leaflets in the anterior portion of the tube, which is kept cool.

If alizarin is treated with nitrous acid, the result is anthraquinon.

In order to effect this reaction, alizarin is dissolved in concentrated sulphuric acid, and nitrate of potassa is gradually added or nitrous acid is conducted into the solution. The original bright-red colour of the solution soon passes into a brown; and if a drop of the mixture is placed in dilute soda-lye, there appears no longer the violet colour of alizarin but a yellowish-red. On further addition of nitrous acid, the colour of the solution becomes finally a deep pure yellow, and a drop no longer gives any colouration with alkali. On dilution with water a precipitate is formed, which on filtration appears with a greenish-yellow colour, and with zinc powder and soda-lye produces the red reaction of anthraquinon. It is capable of sublimation, and has the same melting-point as anthraquinon. The filtrate is a pale yellow, and if mixed with carbonate of lime and the lime thrown down with carbonate of soda, and the filtrate evaporated to dryness, an orange-yellow salt is obtained, which, if melted with alkali, indicates a monosulpho-anthraquinon compound. The course of the reaction may be as follows:—



Natural alizarin yields the same results, and the above-mentioned colour reaction indicates that the alizarin is first converted into monoxanthraquinon and then into anthraquinon.

Purpurin and isopurpurin, if submitted to the same reaction, yield the same ultimate result, but do not appear to be first converted into alizarin.

In many respects alizarin behaves as an acid, in which two atoms of hydrogen can be replaced by a metal. The potassium, sodium, and ammonium salts are readily soluble

in water; the rest either quite insoluble or very sparingly soluble. The potash and soda salts are of a deep violet colour, but if their aqueous solution is exposed to the air for some time it becomes red. This is due to the formation of potassic or sodic carbonate, in which alizarin dissolves with a red colour. The soda salt may be obtained in crystals by dissolving alizarin in hot alcohol and mixing this liquid with a slightly alcoholic solution of sodic hydrate. The mixture is then allowed to cool to 35°, and ether is added, when sodic alizarate is deposited in fine needles of a deep violet, almost black colour.

Phosphates, pyrophosphates, arseniates, arsenites, borates, silicates, &c., indeed all alkaline salts with a basic reaction, dissolve alizarin with a reddish-violet colour, giving up a part of their base in the alizarin.

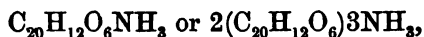
Eugene Schall proposes to use alizarin as an indicator in titration. A solution of alizarin is far more sensitive than one of litmus, as by its means we may recognise  $\frac{1}{300,000}$  of alkali, whilst a neutral solution of alizarin strongly diluted is turned yellow by 0.0007 of hydrochloric acid.

The solution of alizarin is prepared by boiling excess of alizarin with a drop of carbolic acid in potassa-lye and filtering when cold. Such a solution keeps well, but without the carbolic acid it is decomposed in a few weeks. The reaction is more marked if we first supersaturate with an acid and then titrate back with an alkali. As soon as the yellow colour passes into rose, the acid is neutralised and the slightest excess of alkali is indicated. If we saturate an alkaline solution with an acid, the reaction is less striking, and traces of lime, alumina, &c., have a very disturbing effect.

#### *Ammonium Alizarate and Alizaramid and Alizarin.*

The transformation of alizarin by means of ammonia has been examined by Schützenberger and Paraf; that of pur-

purin by Stenhouse and Schützenberger. The latter chemist named the products amids, but ascribed to alizarin the formula—

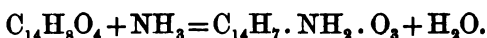


according to which the compound of alizarin and ammonia would be formed without the accession of water. This very improbable formation, according to him, holds good also in the action of ammonia upon quercetin and haematoïn. Stenhouse proposes for purpurin the formula  $\text{C}_{33}\text{H}_{20}\text{N}_2\text{O}_{10}$ . Schützenberger regarded it as a true amid, with the formula  $\text{C}_{20}\text{H}_{13}\text{NO}_6$ . Schützenberger and Paraf, however, have probably, as would appear from their description, operated upon an impure substance.

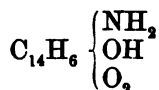
To obtain accurate results it is needful above all things to set out with a pure alizarin. Liebermann and Troschke purified ordinary commercial alizarin by Auerbach's method, i.e. by dissolving it in dilute soda-lye and treatment with carbonic acid. If this process is several times repeated, and the resulting alizarin is then repeatedly extracted with baryta-water, it is ultimately obtained in a state of purity.

Liebermann and Troschke acted upon alizarin with ammonia at temperatures between  $150^\circ$  and  $200^\circ$ . If the action is more prolonged, the same results are obtained at  $100^\circ \text{C}$ . If very concentrated solutions are employed, only a single product is formed by the reaction. This is precipitated in reddish-brown flocks on the addition of acids to the purple solution. In order to purify it from a little unmodified alizarin as well as from traces of another product of the reaction, the precipitate is treated with baryta-water, when only the barium salt of the new compound dissolves with a blue colour. The solution is again precipitated with an acid, and the precipitate is recrystallised from boiling alcohol. From this solution the new compound separates in the form of fine brown needles, possessing, when dry, a metallic lustre. They dissolve in alcohol relatively very easily with a brownish-

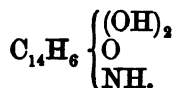
yellow colour, and are readily soluble in alkalis and alkaline earths even in the cold, forming purple solutions. They melt at about  $250^{\circ}$  to  $260^{\circ}$ , and, if cautiously heated, sublime without decomposition. This compound is formed in accordance with the equation—



According to the empirical formula it is doubtful whether an OH of the alizarin has been replaced by  $\text{NH}_2$ , or an O of the quinon group by NH, and consequently whether its rational formula is

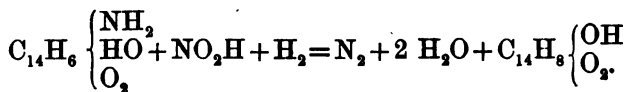


or—



Further investigations have proved that the former view is correct. This appears from the composition of the barium salt obtained by boiling with carbonate of baryta, which is  $(\text{C}_{14}\text{H}_8\text{NO}_3)_2\text{Ba}$ , and shows only one OH in the combination; whilst the second formula would have to contain two atoms of hydrogen replaceable by barium, and consequently almost double the amount of that element. The barium salt, moreover, even on careful evaporation, is resolved into  $\text{BaCO}_3$  and free amid by absorbing  $\text{CO}_2$ .

A further argument for this constitution is offered by the decomposition of the substance by nitrous acid in a hot alcoholic solution. It is entirely converted into oxyanthraquinon, completely identical with that already described, whilst nitrogen gas escapes. The origin of the oxyanthraquinon can be explained in accordance with the first formula.

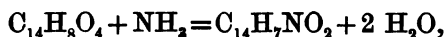


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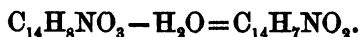
Dilute alkaline solutions of alizarinamid are not changed on boiling. If melted with potash, there is formation of alizarin, but the change takes place slowly. Alizarin is obtained very completely by the action of pure hydrochloric acid. This, on boiling, dissolves a considerable quantity of the amid unchanged; but if heated to  $250^{\circ}$ , pure alizarin is formed, which fills the tube with long orange needles resembling sublimed alizarin.

Ammonia acts in the same manner upon purpurin, forming purpurinamid or amidobioxanthraquinon.

If the tubes in which alizarin is exposed to the action of ammonia are filled, not with a solution of an ammoniacal salt, but with large quantities of the flocculent precipitate of alizarin with the addition of strong ammonia, there is formed along with a predominating quantity of the above-mentioned product a second also, which is deposited in the tube in dark crystals, whilst alizarinamid remains in solution. It is an ammonia compound, which loses ammonia if boiled with dilute soda-lye, if heated with hydrochloric acid, and if evaporated to dryness at  $120^{\circ}$ . After digestion with dilute hydrochloric acid, the compound has the formula  $C_{14}H_7NO_3$ , and is therefore formed according to the equation—

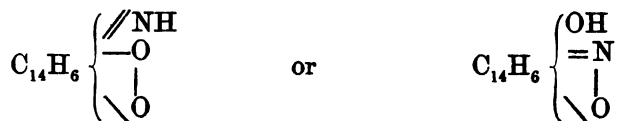


or is obtained from alizarinamid as an intermediate product of the loss of water.

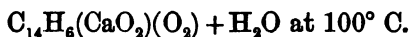


It crystallises in forms closely resembling those of the foregoing compound, is scarcely soluble in ammonia; dilute alkalis dissolve it slightly in the cold, but freely and with a purple colour at  $100^{\circ}$ . Acids precipitate it from this solution in red flocks, resembling alizarinamid. On treatment with baryta water, however, the latter yield an insoluble deep-violet salt of baryta. Liebermann and Trauschke gave this

compound the name of alizarinimid, and its composition may be represented either by the formula—

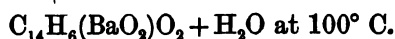


*Calcium Alizarate.*



This salt is obtained by the decomposition of the potash salt with chloride of calcium. It is insoluble in water; of a beautiful purple violet when moist, but almost black when dry, as it loses its crystalline water. The dry salt becomes yellow and of a metallic lustre if heated in a silver capsule. The affinity of alizarin for calcium is very great, and its alkaline solutions are completely precipitated by chloride of calcium or hydrate of lime.

*Barium Alizarate.*



This compound, like the lime salt, is obtained by mixing the alkaline solution of alizarin with chloride of barium. It is deep violet when moist, almost black when dry, and sparingly soluble in water. If heated with very concentrated potash-lye, it gives up alizarin to the alkali; but on the addition of water barium alizarate is again deposited. If, however, alcohol is used instead of water, the potassium alizarate remains in solution, and is not precipitated as barium alizarate even by an excess of alcohol.

It was formerly supposed that barium alizarate, if submitted to dry distillation, yielded a sublimate of anthraquinon. It appears, however, that this anthraquinon was merely an



impurity of the artificial alizarin which had been precipitated along with the barium alizarate.

*Aluminium Alizarate*,  $(C_{14}H_6(O_2)_3Al_2O_6$  (?).

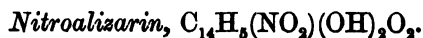
This compound is obtained by precipitating an alkaline solution of alizarin with alum or hydrate of alumina, or by mixing the alcoholic solution with gelatinous alumina. It may also be obtained by boiling acetate of alumina (red liquor) or sulphate of alumina with very dilute alizarin paste. It is a very fine red, more or less inclining to a rose.

*Lead Alizarate*,  $C_{14}H_6(PbO_2)_2O_2$ .

This compound is obtained from the alcoholic solution of alizarin by mixing it with an alcoholic solution of sugar of lead. It then appears as a precipitate varying from purple red to dark red. But if an alkaline solution of alizarin is mixed with aqueous sugar of lead, the precipitate is more violet.

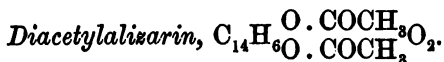
Almost all other salts can be obtained by double decomposition of an almost saturated alkaline or ammoniacal solution of alizarin with the corresponding soluble metallic compounds. The following table shows the colour of the different metallic alizarates as precipitated :—

|                          |   |   |   |                            |
|--------------------------|---|---|---|----------------------------|
| Strontium chloride       | . | . | . | violet, slightly reddish.  |
| Magnesium sulphate       | . | . | . | blueish violet.            |
| Magnesium chloride       | . | . | . | dark violet.               |
| Ferrous chloride         | . | . | . | blackish violet.           |
| Ferric chloride          | . | . | . | brown black.               |
| Chromic chloride         | . | . | . | brownish violet.           |
| Copper sulphate          | . | . | . | brownish-red violet.       |
| Lead basic acetate.      | . | . | . | violet, slightly brownish. |
| Mercurous nitrate.       | . | . | . | dark-violet black.         |
| Mercuric chloride.       | . | . | . | dark violet.               |
| Copper, ammonio-chloride | . | . | . | deep violet.               |
| Tartar emetic            | . | . | . | reddish-yellow violet.     |
| Stannous chloride.       | . | . | . | reddish violet.            |
| Stannic chloride         | . | . | . | pure violet.               |

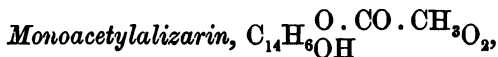


Perkin obtained this compound from diacetylalizarin,  $C_{14}H_6(C_2H_3O)_2O_4$ , by the action of nitric acid. Rosenstiehl gives the following method for its preparation. Large flasks are coated internally with alizarin paste, which is allowed to dry, and they are then filled with the fumes of hyponitrous acid. After a few minutes the flasks are rinsed out with water and the insoluble part treated with soda. The soda salt of nitroalizarin dissolves in pure water, but is very sparingly soluble in presence of excess of alkali. Nitroalizarin is also obtained if we dissolve alizarin in glacial acetic acid and add nitrite of potassa. The nitro-compound is further obtained by treating alizarin dissolved in alcohol with nitrous acid; but in both these cases the yield is unsatisfactory, as a part of the alizarin is destroyed. Free nitroalizarin crystallises from chloroform in orange-red scales with a green reflection. It is capable of sublimation, but a large portion is destroyed. The compound which it forms with metallic oxides is more permanent than the corresponding alizarin derivatives. With iron mordants it gives a dark-red violet, but with aluminous mordants a fine orange-red.

On reduction, this compound yields, according to Perkin, amidoalizarin, but according to Rosenstiehl it forms two colouring matters which have not been closely examined.



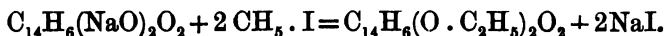
This compound is obtained by heating alizarin with anhydrous acetic acid at  $160^\circ \text{C}$ . From alcohol it is obtained as an amorphous powder.



crystallises in golden yellow scales, and, like diacetylalizarin, is easily decomposed by alkalis.

*Biethylalizarin*,  $C_{14}H_6(C_2H_5O)_2O_2$ .

This compound was obtained by Schützenberger, on heating iodide of ethyl with sodium alizarin.



Iodide of ethyl and alizarate of sodium are heated in closed tubes to 120°. It is a clear yellow liquid, insoluble in water, but soluble in alkalis.

*Bibenzoylalizarin*,  $C_{14}H_6(OC_7H_5O)_2O_2$ .

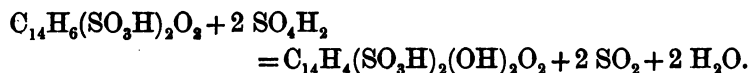
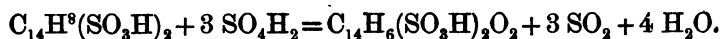
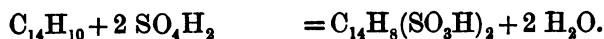
According to Schützenberger, this is obtained by heating chlorbenzoyl with alizarin in sealed tubes to 190° C. It is yellow, insoluble in water, soluble in alcohol, out of which it crystallises. In the cold it is insoluble in alkalis and ammonia. If heated with alkalis, it is decomposed into alizarin and benzoic acid.

*Sulphalizarinic Acid*.

Alizarin dissolves in sulphuric acid at moderate temperatures, but is precipitated unchanged on the addition of water. But if the temperature is raised, nothing is precipitated on the addition of water, the alizarin having been converted into a sulpho-acid. The acid is best precipitated from the solution with carbonate of lead, and the precipitate is decomposed with sulphuretted hydrogen, when the free acid is obtained in solution. With baryta and sugar of lead it yields a reddish-violet precipitate. In water the acid dissolves in every proportion with a yellow colour, and in potash-lye with a beautiful red. If it is melted with potash, which requires great care to avoid over-heating, the melt takes a violet colour. If supersaturated with acid, we obtain a precipitate which partly disappears on washing.

The residue remaining on the filter yields, on sublimation, a small quantity of a sublimate consisting of yellowish crystals, which dissolve in alkali with a violet colour. Trihydroxylanthraquinon is certainly formed in this process.

Very similar to this sulphalizarinic acid is the sulpho-acid obtained on heating anthracen to 240°–250° with sulphuric acid. If this acid is shaken with ether, the ethereal liquid drawn off and shaken with alkali, the latter takes a blue-violet colour. If the crude sulpho-acid is neutralised with lime for purification, the sulpho-compound of lime separated from the gypsum by filtration, and the solution decomposed with carbonate of soda, we obtain a deep-red solution of a sulpho-compound of soda, whilst the precipitated carbonate of lime is coloured a deep violet-blue. On melting the red sulpho-salt of soda with alkali, we obtain a violet solution, from which acids precipitate only a very little flocculent matter. If the melt is not precipitated till it has grown cold, we obtain more flocks, which, however, chiefly dissolve on washing. Perhaps the sulphuric acid has an oxidising effect upon the anthracen, so that sulphoalizarinic acid is formed directly. The transformation may be represented by the following equations :—



### *The Isomers of Alizarin.*

According to the formula of anthraquinon now universally assumed as correct, 10 isomeric bioxyanthraquinons are possible, of which nine are known, although not with sufficient accuracy. These are anthraflavic acid, isoanthraflavic acid, anthraxanthic acid, alizarin, quinizarin, chrysazin,

frangulic acid, xanthopurpurin, and isalizarin. Concerning the structure and the position of the hydroxyls, little is known; and only in two, alizarin and quinizarin, can its position be given with certainty. Some of these isomers are true colouring-matters, that is, they dye mordanted tissues, whilst others do not. If we compare these bioxyanthraquinons with the mono- and trioxyanthraquinons, we find a very interesting agreement. The two monoxyanthraquinons known to us, oxyanthraquinon and erythroxyanthraquinon, are not dyes; alizarin and quinizarin, probably also xanthopurpurin, are dyes, and the trioxyanthraquinons hitherto known are all dyes. Concerning alizarin and quinizarin, we know with certainty that both the hydroxyls are contained in *one* benzol-ring; in the trioxyquinons, two hydroxyls are always present in one benzol-ring. Hence the remarkable circumstance seems to appear, that an oxyanthraquinon derivative is only then a dye when at least two hydroxyls are contained in one benzol nucleus. Hence, xanthopurpurin may perhaps be the anthraquinon derivative corresponding to resorcin, whilst in all the other isomers the hydroxyls are distributed in both the benzol-rings.

*Quinizarin*,  $C_{14}H_8O_4(1\cdot4)$ .

This substance was first obtained by Grimm according to Baeyer's method, the action of anhydrous phthalic acid upon phenols, i.e. in this case by heating a mixture of hydroquinon, phthalic acid, and sulphuric acid. If the melt is heated to  $130^{\circ}$ – $140^{\circ}$  C., two bodies are formed—a phthalein similar to phenol-phthalein, and a red colouring-matter isomeric with alizarin. In order to isolate the latter body, quinizarin in a state of purity, the crude melt is extracted, first with boiling water, and then with absolute alcohol, the latter extract being then precipitated with water. Or the melt is treated with benzin (boiling-point  $110^{\circ}$ – $120^{\circ}$ ), which

dissolves quinizarin readily, and phthalein but sparingly. It is purified by crystallisation from alcohol and ether. Not merely hydroquinon, but all the substances which produce it, when heated with sulphuric acid, yield quinizarin. Such, e.g., is the behaviour of quinic acid, which, if heated with sulphuric acid, yields  $\alpha$ -bisulphohydroquinonic acid: further, the thiochronate of potassa, from which Graebe's  $\beta$ -bisulphohydroquinonic acid is first formed. The sulpho-acids themselves yield this compound; but it is remarkable that the two isomeric bisulpho-acids produce exactly the same quinizarin. If we assume that on the displacement of the two sulpho-groups phthalein takes their place, we must conclude from this behaviour that one of the two isomeric bisulpho-acids, on heating with sulphuric acid, is converted into the other.

Quinizarin crystallises from ether in orange leaflets, but from benzin and alcohol in deep-red needles. From the alcoholic solution it is precipitated in yellowish-red flocks on dilution with water, which, if heated to  $100^{\circ}$ – $110^{\circ}$ , become dark-red and crystalline. The solutions in ether and sulphuric acid are distinguished by a greenish-yellow fluorescence. The ethereal solution appears brownish-yellow by transmitted light; the sulphuric solution has a peculiar violet colour, which, on dilution, passes into a pale onion-red. A similar fluorescence is displayed by the munjistin obtained by Stenhouse from rubia munjith, a compound which possibly stands in the same relation to quinizarin as does purpurin to alizarin.

When heated, quinizarin sublimes in paler or darker needles and plumose crystals resembling alizarin, whilst a shining carbon is left behind. The melting-point of the sublimed body is from  $194^{\circ}$ – $195^{\circ}$ ; that of the crystals obtained from alcohol  $192^{\circ}$ – $193^{\circ}$ .

With alkalis quinizarin yields blue solutions, with a faint violet cast; the ammoniacal solution displays a violet colour. It is most distinctly produced by the alkaline carbonates.

With baryta this dye forms a beautiful violet-blue compound; with alumina it yields a red lake, with a violet cast; the magnesium compound is a deep violet-blue. The faintly alkaline solution is precipitated of a brownish-red by ferric chloride, and of a dull red by sugar of lead.

If the alcoholic solution is allowed to stand for some time, it becomes gradually decolourised, whilst a deep blue-violet—sometimes black—precipitate is deposited, which redissolves in alcohol with a blue colour. At a boiling heat the alkaline solution is decolourised by zinc powder, but resumes its original colour on exposure to the air.

Quinizarin is not merely isomeric with alizarin, but is most closely related to it, since it is a derivation of anthracen, differing merely in the position of the hydroxyls (1·4), which, in alizarin, are 1·2. If the vapours of quinizarin are passed over heated zinc powder, we obtain white shining leaflets, melting at 210°–212°, and forming, with picric acid, a red compound. If treated with glacial acetic acid and chromic acid, they form a compound capable of sublimation, melting at 273°, and having the exact appearance of anthraquinon.

Quinizarin behaves with aluminous and iron mordants differently from alizarin. It dyes with difficulty, and produces quite different shades. With aluminous mordants it gives a faint bluish-rose, and with iron a slate-grey. But with a mixture of both—the mordant for alizarin brown—it gives tolerably vivid violet shades, which do not, however, equal the beauty of alizarin violet.

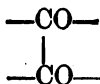
The ethereal and sulphuric solutions of quinizarin display several characteristic absorption-bands.

*Anthraflavic Acid, Isoanthraflavic Acid, and Anthraxanthic Acid.*

Like monoxyanthraquinon, these bodies are the first product of the action of melting alkali upon the bisulpho-acids

of anthraquinon, and as the first must be regarded as the connecting-link between the monosulpho-acid and alizarin, the anthraflavic acids form a transition from the bisulphanthraquinonic acid to the various trioxyanthraquinons, or purpurin.

Concerning the position of the hydroxyls in the three anthraflavic acids, nothing is known with certainty, but the probability is that they are distributed over both benzol-nuclei. It appears as if the property of benzol to form bisulpho-acids only with difficulty extended also to the benzol-rings in anthraquinon. On the first action of sulphuric acid upon anthraquinon, there is formed monosulpho-acid; on further action there are formed, indeed, bisulpho-acids, which, however, on fusion with alkali, yield neither alizarin nor quinizarin (whose position is certainly known), but the anthraflavic acids, and then very easily trioxyanthraquinons. These bisulpho-acids, therefore, correspond to two monosulphobenzolic acids, connected by the group



The trisulpho-acids have hitherto not been examined, but the products arising from their reaction with melting alkali will in any case be colouring-matters.

The body described some time ago by Rosenstiehl as anthraflavon appears to be a mixture of anthraflavic and isanthraflavic acids. As this body is formed by heating metoxybenzoic acid with sulphuric acid, both hydroxyls in anthraflavic acid and isoanthraflavic acid must be distributed in both benzol-rings; and the distinction between these two acids, corresponding to metoxybenzoic acid, and taking the meta-position, may be due to the different position of the connecting CO groups.

As for anthraxanthic acid, very little is known about it,



and information is wanting from which of the isomeric bisulphanthraquinonic acids it is formed.

*Anthraflavic Acid.*

This compound was discovered by Schunck in artificial alizarin. In his first paper on the subject, Schunck gave it the formula  $C_{15}H_{10}O_4$ , and as this was very improbable, on account of its relations to anthracen and alizarin, Graëbe and Liebermann declared it erroneous, and pronounced anthraflavic acid identical with monoxyanthraquinon. Perkin, and also Auerbach, who subsequently examined this compound, proved the correctness of the former assumption, but showed at the same time that anthraflavic acid was a new body, isomeric with alizarin. Schunck, who regarded it as methylalizarin, found, on preparing methylalizarin, and comparing the properties of the two bodies, that his supposition was erroneous.

Anthraflavic acid is formed on melting  $\alpha$ -bisulphanthraquinonate of soda with alkali at a low temperature, and with abundant dilution. The melt, which at the same time contains sulphoxyanthraquinonic acid and flavopurpurin, is boiled with lime, filtered, and the reddish-brown liquid precipitated with hydrochloric acid, when yellow flocks are separated, and may be purified by recrystallisation from alcohol.

Anthraflavic acid may also be obtained from the so-called 'yellow alizarin' of commerce by boiling with lime, but its separation from isoanthraflavic acid is difficult. It has been obtained synthetically by Rosenstiehl on heating metaoxybenzoic acid with sulphuric acid.

Anthraflavic acid is light yellow; it crystallises from alcohol in long yellow needles containing no crystalline water. It is sometimes obtained on the first crystallisation from alcohol in yellow leaflets, but on recrystallisation from

the same solvent it always appears in the form of yellow needles. In glacial acetic acid it is less soluble than in alcohol. In benzol, chloroform, and ether, it is almost insoluble; in concentrated sulphuric acid it dissolves with a yellow colour. In cold baryta-water it is insoluble; sparingly soluble in cold lime-water, and almost insoluble if the liquid is hot. From the aqueous solution of the baryta salt, carbonic acid precipitates free anthraflavic acid. On boiling, however, the salt is reconstituted. Alcoholic sugar of lead dissolves it. The solutions in alkalis and alkaline earths are of a yellowish-red. It sublimes in shining yellow needles or leaflets, and does not dye with mordants. Its melting-point is about  $330^{\circ}\text{C}$ .

*Anthraflavate of Baryta*,  $\text{C}_{14}\text{H}_6\text{BaO}_4 \cdot 2\text{H}_2\text{O}$ .

This compound is obtained by decomposing the lime salt with barium salts, or by boiling anthraflavic acid with the hydrate of baryta. It is very sparingly soluble, and on prolonged exposure to the air it is decomposed. If dried over sulphuric acid, it loses much water, and becomes paler in colour and duller. At  $150^{\circ}$ – $180^{\circ}\text{C}$ . it loses the last two molecules of water.

*Tetrabromanthraflavic Acid*,  $\text{C}_{14}\text{H}_4\text{Br}_4\text{O}_4$ .

This compound is formed when anthraflavic acid is dissolved in alcohol and a large excess of bromine is added. It is almost insoluble in all ordinary solvents.

*Diacetylanthraflavic Acid*,  $\text{C}_{14}\text{H}_6(\text{C}_2\text{H}_3\text{O})_2\text{O}_4$ .

Obtained by Perkin by the action of anhydrous acetic acid upon anthraflavic acid. It crystallises very readily, and melts at  $227^{\circ}\text{C}$ .

*Dimethylantraflavic Acid*,  $C_{14}H_6(CH_3)_2O_4$ .

This compound is formed on heating to  $120^\circ$  C. anthraflavic acid with soda-lye, iodide of methyl, and a little alcohol as diluent. In a few minutes the reaction is complete. A body is formed, insoluble in alkali, which, on recrystallisation from alcohol, is obtained in long, shining, pale-yellow needles. It melts at  $247^\circ$ – $248^\circ$  C.

*Diethylantraflavic Acid*,  $C_{14}H_6(C_2H_5)_2O_4$ .

This compound is formed in the same manner as dimethylantraflavic acid, by means of iodide of ethyl. It is insoluble in water, sparingly soluble in alcohol and ether, more freely soluble in glacial acetic acid and benzol. It dissolves in sulphuric acid with a red colour. This solution displays an absorption-band on the borders of the green and the blue; the further portion of the blue is obscured. It melts at  $232^\circ$  C. If cooled, even rapidly, the solution solidifies in large prismatic crystals.

*Isoanthraflavic Acid*,  $C_{14}H_6O_4$ .

Isoanthraflavic acid is obtained from the  $\beta$ -bisulphanthraquinonate of soda in the same manner as anthraflavic acid is prepared from the  $\alpha$  variety. It also accompanies anthraflavic acid, when prepared from metaoxybenzoic acid.

In order to obtain it from commercial 'yellow alizarin,' this is boiled with lime-water, filtered, the filtrate decomposed with hydrochloric acid, the precipitate collected upon a filter, well washed, and finally treated with cold baryta water, in which isoanthraflavic acid dissolves as a barium salt. On adding hydrochloric acid, we obtain free isoanthraflavic acid. It crystallises from aqueous alcohol in long yellow needles, containing crystalline water. It melts at

330° C., and is more sparingly soluble in glacial acetic acid than in alcohol; almost insoluble in benzol, chloroform, and ether; soluble in sulphuric acid, with a deep-red colour; easily soluble in cold baryta- and lime-water, as also in alcoholic acetate of lead. Free isoanthraflavic acid is precipitated from the aqueous solution of the barytic salt by carbonic acid, which is reformed, however, on boiling. The solutions in alkalis and alkaline earths are of a deep-red colour. It sublimes in shining yellow needles, and does not dye with mordants.

*Isoanthraflavate of Baryta,  $C_{14}H_6BaO_4$ .*

This salt is readily soluble in water, and crystallises with difficulty in dark-red shining needles. On exposure to the air it is readily decomposed. If dried at 150°, it loses its water of crystallisation.

*Tetrabromisoanthraflavic Acid,  $C_{14}H_4Br_4O_4$ .*

This compound is obtained by dissolving isoanthraflavic acid in alcohol, and adding drop by drop a large excess of bromine. In a few minutes the solution congeals to a crystalline paste of yellow needles, sparingly soluble in alcohol, but more freely in glacial acetic acid.

*Diacetylisoanthraflavic Acid,  $C_{14}H_6(C_2H_3O)_2O_4$ .*

This acid is formed by the reaction of anhydrous acetic acid upon isoanthraflavic acid at 160°–180°, and is sparingly soluble in alcohol, but more easily in glacial acetic acid. From the former solvent it is obtained in pale-yellow microscopic crystals. They frit together at 175°, and melt completely at 195°. If heated with alcoholic potassa, the acetyl-group is separated.

*Diethylisoanthraflavic Acid*,  $C_{14}H_6(C_2H_5)_2O_4$ .

To obtain this compound, isoanthraflavic acid is heated to  $120^\circ$  with soda-lye, iodide of ethyl, and a little alcohol. In a few hours the reaction is completed, and a body is formed, insoluble in potassa-lye, and which is obtained in long, shining, pale-yellow needles on recrystallisation from alcohol. It is quite insoluble in water, sparingly soluble in alcohol and ether, more freely in glacial acetic acid and benzol. It dissolves in concentrated sulphuric acid with a reddish-violet colour. The solution shows two indistinctly-developed absorption-bands in the green and the yellow. If the solution is more concentrated, an absorption-band appears also in the blue. The melting-point of this compound is at  $193^\circ$ – $194^\circ$ .

*Anthrazanthic Acid*,  $C_{14}H_8O_4$ .

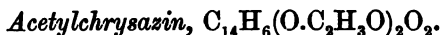
This acid was discovered by Ulrich and Perger in the 'new red' of the alizarin manufactory of Przibram and Co., and can be obtained by the sulphation of chemically pure anthracen only under certain circumstances. According to statements hitherto published, this acid takes up no water of crystallisation; it is insoluble in cold glacial acetic acid, and sparingly soluble even at the boiling-point; sparingly soluble in cold alcohol, but more readily with the aid of heat. From hot alcohol it crystallises in small gold-coloured needles, which are deposited as the solution cools. It is insoluble in benzol, and more readily soluble in ether than in alcohol. In concentrated sulphuric acid it dissolves with a red colour. It is almost insoluble in cold baryta-water, but dissolves in the same liquid when hot, and crystallises on cooling in red-brown needles. The ammoniacal solution of the acid is completely decomposed and precipitated by baryta-water, an excess of which renders it insoluble. In hot lime-water it is

sparingly soluble, more easily when cold. It is very slightly soluble in cold alcoholic sugar of lead. The solution in alkalis is of a fine orange colour, and after a short time, if the solutions are not too dilute and if the alkali is in excess, the salt crystallises out in splendid felted needles, varying in colour from orange to the redness of chromic acid. If the solution is sufficiently concentrated, it becomes gelatinous. The pure soda salt is easily recrystallised. It is soluble in alcohol, from which it crystallises on the addition of ether. If heated in a tube with access of air, a portion is decomposed, whilst the rest sublimes in splendid iridescent yellow leaflets. If melted with alkali, it undergoes no change, and does not dye with mordants.

*Chrysazin*,  $C_{14}H_8O_4$ .

This body was obtained from hydrochrysamid by Liebermann and Giessel. A sulphuric solution of hydrochrysamid is mixed with water till it has a pasty consistence. It is kept cool with snow, and a current of nitrous acid is passed through it till the paste liquefies, turns a cherry-red, and till nitrous vapours escape unabsorbed. The mass is then introduced into well-cooled alcohol with constant stirring, and the brown-red precipitate of a diazo-compound is quickly removed by filtration. It is next heated with alcohol to  $60^\circ$  till nitrogen and aldehyd begin to escape, and after the reaction is completed it is boiled for some time. A considerable quantity of a nitrogenous substance insoluble in alcohol is then filtered off, and the alcoholic filtrate is precipitated with water, agitated with ether, evaporated to dryness, and recrystallised from alcohol or acetic acid. Chrysazin is obtained from glacial acetic acid in red-brown, shining needles, but from alcohol in golden-yellow leaflets. Both forms, however, are identical, and are respectively capable of conversion. It melts at  $191^\circ$  C., dissolves in alkalis with an orange colour, but only in mere traces in the alkaline carbo-

nates and in ammonia. Salts of lime and baryta produce red precipitates. It does not dye with mordants. If heated with zinc-powder it yields anthracen. From chrysazin are derived chrysammic acid, tetranitrochrysazin, and the tetramido (or diamidoimido) chrysazin of hydrochrysamid.



It is obtained on heating chrysazin with anhydrous acetic acid at  $170^\circ$ . It crystallises from alcohol in yellowish leaflets resembling benzoic acid; it is capable of sublimation, and melts at  $226^\circ$ – $230^\circ$ .

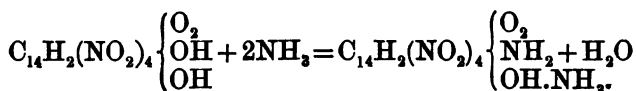


This compound was first obtained by Braconnot on treating aloes with nitric acid, and is also formed, according to W. De la Rue and H. Müller, from chrysophanic acid by the action of the same reagent. More recently it has been prepared by Liebermann and Giessel by the nitration of chrysazin, and submitted to a closer examination. By its preparation from chrysazin it has been proved to be a derivative of anthracen. De la Rue and Müller, who advocated the duplication of the formerly assumed formula  $C_7H_2N_2O_6$ , regarded chrysammic acid as tetranitrochrysophanic acid. But the researches of Liebermann and Fischer, which proved that chrysophanic acid is a derivative of methylanthracen, and the most recent investigations on chrysazin, have demonstrated this view as untenable.

Chrysammic acid, as Graebe and Liebermann formerly declared, must be regarded as a tetranitrobioxanthraquinon,  $C_{14}H_2(NO_2)_4(OH)_2O_2$ . The two hydrogen atoms of the hydroxyls can be replaced by metals, yielding the salts which have been examined in detail by Schunck, Mulder, Stenhouse, and Müller, and which have the general formula,

$C_{14}H_2(NO_2)_4(OM)_2O_2$ . This formula also renders intelligible the composition of the body known as chrysammid, and obtained by the action of ammonia upon chrysammic acid. The analyses of Schunck and Mulder agree well with the formula proposed by the latter,  $C_{14}H_3N_4O_{11}(C=6 \ O=8)$ , and cannot therefore be harmonised with the correct atomic weight of oxygen on the assumption of only 7 atoms of carbon in chrysammic acid. Gerhardt, therefore, regarded the above compound as a mixture of  $C_7N_3H_4O_8 + C_7N_3H_4O_6$ .

According to present views the compound in question is considered not as chrysammid, but as the ammon-salt of amidotetranitrochrysazin,  $C_{14}H_2(NO_2)_4(H_2N)(OH)O_2$ . The ammon-compound is formed in accordance with the following equation:—



This equation agrees also with the amount of water obtained on passing ammonia over chrysammic acid. The behaviour of the compound is also rendered intelligible by this view. Whilst on treatment with strong acids chrysammic acid is re-formed, there is obtained by means of dilute hydrochloric or sulphuric acid an intermediate link containing more nitrogen than chrysammic acid and having the character of an acid. This is evidently free chrysammidic acid,  $C_{14}H_2(NO_2)_4(NH_2)(OH)O_2$ , which Schunck obtained not perfectly free and described as amido-chrysammic acid. As this chemist observed, the salts of this acid are formed also from the ammonia-salt on mixing it with the soluble salts of the respective metals.

For the preparation of chrysammic acid there are various methods. According to Stenhouse and Müller, the most abundant yield is obtained as follows: 6 vols. of nitric acid of spec. grav. 1.36 are placed in a retort provided with a good condenser. The acid is heated almost to a boil and



2 parts of Socotra aloes in small fragments are gradually added. At the beginning the additions must be made cautiously, avoiding too strong a heat. But when a considerable proportion of the aloes has been added the temperature must be raised, and the acid which has passed over is returned into the retort. After the whole of the aloes have been put in, the heat is continued for ten hours, but in the latter part of the time the distillate is no longer returned, so that the contents of the retort are finally reduced to half of the original volume. To the residue three parts of fresh nitric acid are gradually added, and the digestion is continued for six to seven hours longer, the acid being finally distilled off. The contents of the retort are now introduced into about 4 parts of water and well stirred, so that oxalic acid is dissolved whilst picric and chrysophanic acids remain insoluble. The two latter are collected again, almost dried, and placed in a retort with 1 part of nitric acid of spec. grav. 1.45 and digested six to eight hours. The residue, consisting of picric, aloetic, and chrysammic acids, is washed with boiling water by decantation till the washings appear of a flesh colour and the picric acid is removed. The residue, aloetic and chrysammic acid, is dried, digested again in the retort with 1 part of strong nitric acid, the product washed with hot water till the washings run off flesh coloured, then boiled for a few minutes with 4 parts of water, and filtered. The last operation is repeated three or four times till the filtrate appears light-red instead of purple-red. It is then extracted with boiling water, to which a slight excess of chalk has been added, when the contents of the vessel take a deep-red or purple-red colour. On cooling, there appear on the sides small needles of chrysammate of lime. They are collected and recrystallised from a mixture of equal parts of alcohol and water. The crude salt is purified by repeated crystallisation alternately from boiling water and from alcohol. Pure chrysammic acid is obtained from the concentrated boiling

solution of the lime-salt by the addition of a slight excess of nitric acid. On cooling, the free acid is thus obtained in moderately large golden scales, resembling iodide of lead in aspect.

Chrysammic acid is formed also by treating chrysophanic acid with nitric acid.

Tilden proposes the following method for the preparation of chrysammic acid:—A brown, but not too dark, kind of Barbadoes aloes is agitated with 7 to 8 parts of boiling water, to which a little hydrochloric acid has been added. The liquid is then allowed to stand for twenty-four hours, decanted, and evaporated to a syrupy consistence. This syrup is allowed to stand for a day or two, when a granular mass of crystals separates, and is freed from the mother-liquor by pressure. We thus obtain 20 to 25 per cent. of crystals, which Tilden names barbaloin. They are dried, powdered, and mixed with about 6 parts of fuming nitric acid, to which water is afterwards added. Light-yellow crystals are thus obtained. The two acids are separated by treatment with acetate of potassa.

Chrysammic acid forms clinorhombic crystals, which appear of a golden-yellow by transmitted light. This colour is resolved by the dichroscope into a reddish-brown and a yellowish-green. The reflected light, on the other hand, is a brilliant bluish-white, and consists of two rays polarised at right angles, one of which appears constantly bluish-white at every change of incidence, whilst the other changes to yellow, orange, reddish-blue, and to violet. This circumstance may be connected with the polychroic character of the crystals, if strongly magnified, but viewed by common light. Whilst the main colour is a golden-yellow, some parts of the crystal appear greenish-yellow, green, blue-green, reddish-yellow to brownish-red, a phenomenon which finds its explanation in a combination of the transmitted light with the rays reflected from the interior of the crystal.

Chrysammic acid has a bitter taste; it is sparingly soluble in cold and more freely in hot water; the solution is yellowish-red or purple-red, according to the degree of concentration; it dissolves more readily in spirit of wine (in 70–80 parts of cold alcohol) and in ether, as well as in dilute acids and saline solutions.

If gradually heated, chrysammic acid melts and is decomposed. If rapidly heated, it detonates with violence. Fuming nitric acid, with heat, converts it into picric acid; on distillation with chloride of lime and water, or treatment with chlorate of potash and hydrochloric acid, there is formed chloropicrin. Concentrated sulphuric acid acts upon it only in heat, forming chrysoiodin, a violet body, insoluble in water.

If boiled in dilute sulphuric acid, on the addition of water pure chrysammic acid is precipitated as a greenish powder, which Robiquet took for a product of decomposition, and named chrysammelid.

Aqueous sulphide of potassium at a boiling heat reduces it to a blue solution of hydrochrysammid.

If heated with aqueous cyanide of potassium, chrysammic acid is converted into chrysocyaminic acid.

The ammoniacal solution of chrysammic acid is coloured first blue and then brown by sulphurous acid. Stannous chloride colours the solution of the acid violet, but it becomes blue if heated. If an excess of the tin-salt is employed, hydrochrysophanate of tin is thrown down as a deep-violet powder, but chrysammic acid is reformed on heating with nitric acid.

If boiled with potassa-lye, chrysammic acid turns brown, and on the addition of acids chrysatinic acid is precipitated— $C_{12}H_6N_2O_{10}$  (Schunck), or  $C_{24}H_6N_3O_{12}$  (Mulder). This acid is somewhat soluble in water, but is precipitated from the solution by mineral acids; it forms, with the alkalis and alkaline earths, salts, soluble in water, which are precipitated by the salts of silver and lead.

Ammonia, dry or aqueous, combines with chrysammic acid, with elimination of water and formation of chrysammidic acid,  $C_{14}H_2(NO_2)_4(NH_2)(HO)(O_2)''$ .

Chrysammic acid combines with bases, and decomposes carbonates and acetates, sometimes even chlorides and sulphates. The salts have the composition,  $C_{14}H_2(NO_2)_4(MO)_2(O_2)''$ ; they are coloured, and for the most part sparingly soluble in water; most of them crystallise in needles or scales of a golden-green metallic lustre; they lose their crystalline water at  $120^\circ$ – $150^\circ$ , and often detonate if rapidly heated. Their optical properties have been examined by Brewster and Haidinger.

*Chrysammate of Potassa*,  $C_{14}H_2(NO_2)_4(O_2)''(KO)_2 + 3HO$ .

This salt is prepared by triturating the acid with carbonate of potassa, and dissolving in hot water, or by boiling the acid with acetate of potassa. It forms golden-green scales; or, if separated by rapid cooling, it is a carmine-red powder, which, under the microscope, displays a crystalline texture. It dissolves in 1250 parts of cold water, but is readily soluble in hot water, with a red colour; if dried at  $120^\circ$ , it is rendered anhydrous; at higher temperatures it detonates. The salt readily adheres to glass on pressure, and displays then an interesting dichroism, both by transmitted and by reflected light. By transmitted light, polarised in the direction of the film, it appears flesh-coloured or blood-red; if polarised perpendicularly to the plane of the film, it is carmine-red to crimson. By reflected light, polarised in the plane of the film, it appears steel-grey to violet; or at a greater angle of incidence, violet to deep indigo-blue. If the light fall perpendicularly upon the film, the colour appears of a brassy-yellow, or at a greater angle of incidence, metallic-green to steel-blue.

*Chrysammate of Soda*,  $C_{14}H_2(NO_2)_4(O_2)''(NaO)_2 + 3H_2O$ .

Prepared in the same manner as the potassa-salt, which it closely resembles, and is as sparingly soluble.

*Chrysammate of Baryta*,  $C_{14}H_2(NO_2)_4(O_2)''(BaO_2)$ .

Obtained by decomposing the hot aqueous solution of the potassa-salt with solution of chloride of barium. It is a purple-red powder, consisting of microscopic crystals, and insoluble in water.

*Chrysammate of Lime*,  $C_{14}H_2(NO_2)_4(O_2)''(CaO_2)$ .

Obtained in the same manner as the barytic salt. A dark-red powder, sparingly soluble in water, more freely in boiling alcohol, from which it crystallises in red needles.

*Chrysammate of Magnesia*,  $C_{14}H_2(NO_2)_4O_4Mg + 5H_2O$ .

Splendid crystals, of a reddish-golden lustre, which on drying become of a golden-brown, but if touched with water or breathed upon they return to their original colour by taking up water. According to Mulder, this salt contains  $6H_2O$ .

*Manganous Chrysammate*,  $C_{14}H_2(NO_2)_4(O_2)''(MnO_2) + 5H_2O$ .

Forms golden-yellow scales of a fine red by transmitted light, soluble in water and dilute alcohol.

The *ferrous* salt is deep violet, and soluble.

The *zinc* salt is purple-red, crystalline, and sparingly soluble.

*Chrysammate of Lead*,  $C_{14}H_2(NO_2)_4(O_2)''(PbO_2) + 5H_2O$ .

A brick-red insoluble salt, prepared by the action of the free acid upon sugar of lead. On decomposing sugar of lead

by chrysammate of potassa, there is formed a deep red precipitate of a basic salt,  $C_{14}H_2(NO_2)_4(O)_2''(PbO_2) + PbH_2O_2$ .

*Chrysammate of Copper*,  $C_{14}H_2(NO_2)_4(O)_2''(CuO_2) + 4H_2O$ .

Obtained as a dark-red powder, by decomposing sulphate of copper with the potassa-salt; from hot water it crystallises in dark-purple needles.

*Chrysammate of Silver*,  $C_{14}H_2(NO_2)_4(O)_2''(AgO)_2$ .

Deep violet crystalline needles, sparingly soluble in water.

*Chrysammic Ethylic Ether*,  $C_{14}H_2(NO_2)_4(O)_2''(C_2H_5O)_2$ .

Obtained by introducing the silver-salt into a flask provided with a long condensation-tube, adding 5 parts of iodide of ethyl, and digesting ten to fifteen minutes in the water-bath. The condenser is then replaced by a curved tube, and the excess of iodide of ethyl is distilled off. The residue, which consists of iodide of silver and chrysammic ethyl-ether, is extracted by benzol, which, on cooling, deposits the ether in hard, dark-brown crystals, which are pulverised and recrystallised four to five times with benzol, till the crystals appear of a pale yellow. It is finally obtained pure by recrystallisation from alcohol. In all these operations moisture must be avoided, otherwise the ether is decomposed. It crystallises from alcohol in hard, pale-red needles, and from benzol in hard yellow prisms; in ether it is sparingly soluble, and insoluble in bisulphide of carbon. If enclosed in a tube, it melts, and is decomposed; on platinum-foil it burns quietly.

*Chrysammic Benzoyl ether*,  $C_{14}H_2(NO_2)_4(O)_2(O \cdot C_7H_5O)_2$ .

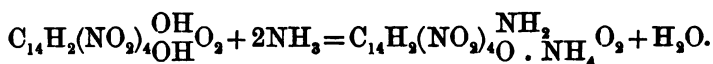
Obtained by heating together chrysammic acid and benzoylchloride. It forms yellow prismatic crystals, insoluble in most liquids.

Chrysammic acid dyes upon silk and wool beautiful shades, varying, according to the mordant, from 'corinthe'-violet (a reddish-brown violet) to blue.

*Chrysammidic Acid*,  $C_{14}H_2(NO_2)_4(NH_2)OH(O_2)''$ .

Discovered by Schunck, who gave it the name of amido-chrysammic acid. He expressed its composition by the formula  $C_{14}H_4N_2O_{11}$ , which agrees well with the numbers which he obtained. Graebe and Liebermann give it the formula  $C_{14}H_6N_2O_{11}$ , and regard it as a derivative of chrysammic acid, one hydroxyl being replaced by an amid group.

It is obtained, according to Schunck, as follows: Chrysammic acid is boiled with aqueous ammonia. The acid dissolves, forming a dark-purple liquid, which, on cooling, deposits crystalline needles of a reddish-brown colour by transmitted light, but by reflected light having the green metallic lustre peculiar to the salts of chrysammic acid. This substance, however, is not chrysammate of ammonia, for on adding an acid this salt is not separated. It is the ammon-salt of chrysammidic acid. The formation of this salt takes place according to the equation:—



If to the hot aqueous solution of this ammon-salt hydrochloric acid or dilute sulphuric acid be added, free chrysammidic acid separates on cooling in dark needles, which, when filtered, washed, and dried, have a deep olive-green colour.

The acid dissolves in water with a dark-purple colour, and is partially reprecipitated by strong acids, with or without the purple colour passing into yellow. On boiling with potassa solution ammonia escapes, and chrysammic acid is reformed. On boiling with nitric acid it is likewise converted into chrysammic acid, with the escape of red fumes. The same

change may be produced by concentrated sulphuric acid, but dilute acids have no action. The salts of chrysammidic acid have nearly the same appearance and the same properties as the corresponding chrysammates. If heated, they detonate with the same violence. They may, however, be easily distinguished from the chrysammates by evolving ammonia, if heated with an alkali. The insoluble salts may be obtained from the potassa-salt by double decomposition, or direct from chrysammidic acid by the addition of ammonia and the soluble metallic compound requisite.

*Chrysammidate of Potassa*,  $C_{14}H_2(NO_2)_4(O_2)(NH_3)(KO)$ .

Obtained by treating the free acid with a cold solution of carbonate of potassa, washing away the excess of alkali with excess of water, and crystallising from boiling water. It crystallises in small needles, of the same metallic-green lustre as the chrysammate of potassa.

*Chrysammidate of Baryta*,  $[C_{14}H_2(NO_2)_4(O_2)NH_2O]_2Ba$ .

If to an aqueous solution of chrysammidate of ammonia chloride of barium is added, no precipitate is formed in the cold, and the liquid retains its purple colour. On prolonged boiling, chrysammidate of baryta is gradually deposited as a dark-red crystalline powder. A long time is required, however, before the liquid loses its purple colour and the chrysammidate of ammonia is completely decomposed. If to a solution of chrysammidate of ammonia there be added chloride of barium, and afterwards ammonia, chrysammidate of baryta is at once precipitated, and the solution becomes colourless. The salt is red and crystalline.



*Hydrochrysammid, Tetramido or Diamidoimido Chrysazin,*  
 $C_{14}H_{12}N_4O_4$ .

This body is a reduction-product of chrysammic acid, discovered by Schunck. He proposed the formula  $C_7H_6N_2O_3$ ; but Graebe and Liebermann double this formula, and deduct 2 atoms H, making it  $C_{14}H_{10}N_4O_6$ . In favour of this view we have not merely Schunck's own analyses, but the formula poorer in hydrogen is supported by the observation of Stenhouse and Müller, that on the reduction of chrysammic acid in closed vessels a colourless substance is formed, which only passes into blue hydrochrysammid on contact with the atmospheric air. The same colourless compound, according to Stenhouse and Müller, is obtained by treating hydrochrysammid with reducing agents. According to Schunck's formula, hydrochrysammid is a tetraoxy-compound,  $C_{14}H_2(NH_2)_2(NO_2)(OH)_4$ ; according to that of Graebe and Liebermann it is a bioxyquinon, or triamidonitrobioxyanthraquinon,  $C_{14}H_2(NH_2)_3NO_2(O_2)OH_2$ . The recent investigations of Liebermann and Graebe have shown that neither of these assumptions is correct, but that all the nitro-groups are replaced by amido-groups, and that the true formula of hydrochrysammid is consequently  $C_{14}H_2(NH_2)_4(OH)_2O_2$ .

Still they admit that a formula which contains, instead of four amido-groups, only two amido- and two imido-groups, is not impossible. According to Schunck's formula, the origin of the colourless reduction-product can only be explained by assuming that the last nitro-group is also reduced. The new formula of Liebermann and Giessel explains the origin of this body very naturally; there is formed by the action of reducing agents a tetramidobioxyhydroanthraquinon, which, like hydroanthraquinon, is immediately oxidised on contact with the air.

Schunck obtains hydrochrysammid as follows:—He pre-

prepares a boiling solution of sulphide of potassium, containing an excess of caustic potassa, and adds chrysammic acid. This dissolves with an intense blue colour, and on cooling there is separated a mass of crystalline needles, blue by transmitted light, but having a red metallic lustre by reflected light. After filtration, washing and drying, they form an indigo-blue, almost black crystalline mass, which is purified by solution in boiling potassa-lye and crystallisation.

Hydrochrysammid can also be obtained by treating chrysammic acid with dilute muriatic acid and zinc, or with hydriodic acid, to which some phosphorus is added, to avoid separation of iodine. If chrysammic acid is suspended in water, and then treated with sodium amalgam, there is formed a purple solution, containing hydrochrysammid.

Hydrochrysammid is perfectly neutral. If heated upon platinum foil, it is decomposed without the slightest detonation, and leaves, if perfectly pure, no ash. If heated in a small glass tube, it yields violet vapours, which condense on the cooler parts of the tube in blue crystals. The larger portion, however, is decomposed with the escape of ammonia and the separation of carbon.

Hydrochrysammid is insoluble in boiling water, and sparingly soluble in boiling alcohol, to which it imparts a slight blue colour. It dissolves in concentrated sulphuric acid with a brown colour, and is reprecipitated on the addition of water. If, however, only a small quantity of water be added, the whole solidifies, forming a mass of long yellow needles of the sulphate.

It is decomposed by boiling nitric acid. If diffused in water through which a current of chlorine gas is passed, it is gradually decomposed and dissolved.

It dissolves in potassa-lye and in alkaline carbonates, the solution having the same colour as sulphindigotic acid; acids reprecipitate it in blue flocks.

If treated with boiling nitric acid, much nitrous acid is

evolved, and on the completion of the reaction a dark-brown liquid remains. On evaporating to remove excess of acid, a brown syrup remains, and on the addition of water a brown powder is deposited. This resembles the brown compound produced by the action of potassa-lye upon chrysammic acid. If this brown powder is filtered off, the evaporation leaves a considerable quantity of oxalic acid. The filtrate from this, if mixed with potassa-lye, smells strongly of ammonia.

*Chrysocyammic Acid.*

The product of the reaction of cyanide of potassium and chrysammic acid. It is obtained by adding 1 part of chrysammic acid to a solution of 2 parts cyanide of potassium in 12 to 15 parts water at about 60°. The liquid becomes hot and evolves ammonia and hydrocyanic acid. After some hours' digestion there is formed an imperfectly crystalline precipitate, which is filtered, pressed, and purified by repeated recrystallisation. Pure chrysocyammic acid is then obtained by solution in dilute nitric acid. When dry it has a metallic lustre, is insoluble in water, but soluble in alcohol. At 120° it loses 3 equivalents of water and detonates when heated. It is a monobasic acid, the general formula, according to Finkh, being  $\text{MO.C}_{18}\text{H}_2\text{N}_3\text{O}_{11}$ . The alkaline salts are crystalline, and soluble in water; most of the metallic salts are insoluble, and are obtained by double decomposition as dark-red crystalline precipitates. The salts detonate when heated as violently as gunpowder.

The potash salt is a dark, crystalline powder, reddish-brown when dry and of a metallic lustre when pulverised. It dissolves in water with an intense deep-violet colour, and loses all its water at 120°.

The ammonium salt is obtained by decomposing the potash salt with sal-ammoniac, and forms dark-green needles.

It is more sparingly soluble and more readily crystallised than the potash salt.

The barium salt is obtained on precipitating the ammonium salt with chloride of barium; it is a red-brown powder, of metallic lustre when pulverised, sparingly soluble in pure water, but insoluble in saline liquids.

The lime salt resembles the baryta salt in its behaviour and mode of preparation.

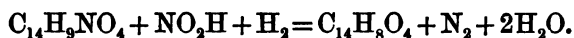
The lead salt is obtained as a voluminous red precipitate, insoluble in water.

The silver salt is obtained from the potash salt by double decomposition. It is a reddish-brown precipitate, which, when dry, has a dark-red brassy lustre.

*Purpuroxanthin*,  $C_{14}H_8O_4$ .

This compound was discovered by Schützenberger and Schiffert in commercial purpurin, and prepared by them from purpurin. It is obtained by allowing ordinary phosphorus to react upon an alkaline solution of purpurin. The latter dissolves without evolution of gas, and the reduction is complete in a few minutes. The colour of the solution passes from violet-red to red, and finally to brown. The product is poured into acidulated water, and the flocculent precipitate is collected and washed.

Another method has been described by Liebermann and Fischer. If nitrous acid is passed through a boiling alcoholic solution of purpurinamid, nitrogen escapes, and a compound is obtained, which, when purified by sublimation, is identical with Schützenberger's purpuroxanthin. It is formed according to the equation :



Schützenberger has also obtained it by the reduction of purpurin with stannous chloride in an alkaline solution.

As Rosenstiehl has succeeded in converting purpuroxanthin into purpurin by oxidation, and as Baeyer has ascertained the constitution of purpurin, it is evident that purpuroxanthin is the third bioxyanthraquinon derivative containing the two hydroxyls in the same benzol-nucleus, for which there remains only the position 1·3. Whilst Liebermann and Fischer state that purpuroxanthin does not dye with mordants, Schützenberger maintains that it dyes a yellow shade.

Purpuroxanthin forms a yellow mass, and sublimes readily in orange-yellow needles resembling pure alizarin.

In alcohol, acetic acid, and benzol, it dissolves readily, and is precipitated by water from its alcoholic solution as a transparent jelly, which gradually condenses into flocks. It dissolves in alkalis with a fine red colour. The lime and baryta salts dissolve in boiling water with an orange-red colour. It dissolves at a boiling heat in alum water, but is almost entirely redeposited on cooling.

If purpuroxanthin is heated with hydriodic acid (boiling-point  $127^{\circ}$ ) and common phosphorus, there is obtained in the first place a substance of a more greenish yellow colour which crystallises from benzol in splendid leaflets. The alkaline solution is brown, and is oxidised on exposure to the air, with reproduction of purpuroxanthin. With aluminous mordants it dyes shades similar to quercitron, and agrees with the formula  $C_{14}H_{10}O_4$ , or  $C_{14}H_{12}O_4$ . On prolonging the action of the hydriodic acid under the same conditions, both the hydrides of anthracen are obtained. If heated with zinc-powder, purpuroxanthin yields anthracen. In a boiling alkaline solution, purpuroxanthin takes up 1 atom of oxygen and purpurin is reproduced.

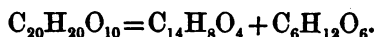
*Frangulin*,  $C_{20}H_{20}O_{10}$ .

This glucoside is obtained from the bark of *Rhamnus frangula*. This is extracted at a boil with ammoniacal water,

the decoction is mixed with hydrochloric acid, the precipitate pressed, and extracted with boiling alcohol and sugar of lead. From the alcoholic solution thus purified the frangulin is precipitated by the addition of more sugar of lead.

The red precipitate is decomposed with sulphuretted hydrogen, and the frangulin is extracted from the sulphide of lead by means of boiling alcohol. The alcohol is mostly distilled off, and from the remainder the frangulin is precipitated by water and obtained in a state of purity by several repetitions of this last operation.

Frangulin forms a yellow mass which appears crystalline under the microscope. It is almost insoluble in cold water, sparingly soluble in cold alcohol and ether, more freely soluble in hot alcohol. Alkalis dissolve it with a fine red colour. The ammoniacal solution is colourless, but soon turns red. It melts at  $226^{\circ}$ , and has the properties of a feeble acid, but its salts have not been obtained. Acids decompose it into frangulic acid and sugar,



*Frangulic Acid,  $C_{14}H_8O_4$ .*

This acid can be obtained also direct from the bark of the rhamnus if it is extracted with water containing caustic soda.

From alcohol it crystallises in orange-coloured quadratic leaflets or needles of the formula  $2(C_{14}H_6)(OH)_2O_2 + 3H_2O$ , which do not become perfectly anhydrous until heated to  $180^{\circ}$ , and melt between  $252^{\circ}$  and  $254^{\circ}$ . It is somewhat soluble in water, chloroform, and benzin; readily soluble in alcohol and ether. Alkalis dissolve it with a fine red colour, but acids separate frangulic acid unchanged from the solution. From a slightly ammoniacal solution it is precipitated by alkaline earths and many metallic salts. Fuming nitric acid dissolves frangulic acid, and a red mass remains on dilution

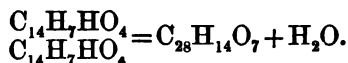
with water. This nitrated frangulic acid is probably the same substance which Casselmann describes as nitrofrangulic acid, and which he obtained along with oxalic acid on heating frangulin with fuming nitric acid. If heated with zinc-powder, frangulic acid yields anthracen.

*Dibromfrangulic Acid*,  $C_{14}H_6Br_2O_4$ .

Obtained by mixing an alcoholic solution of frangulic acid with excess of bromine. It is sparingly soluble in alcohol, and consequently separates from the mixture just mentioned. It forms a bright-red, light crystalline mass, which, under the microscope, appears to consist of fine short needles.

*Difrangulic Acid*,  $C_{28}H_{14}O_7 + 2H_2O$ .

This acid may be regarded as the anhydride of frangulic acid, and it may be formed from 2 mol. of frangulic acid by the elimination of 1 mol. water.

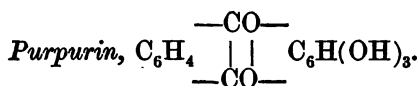


Faust obtained this acid from the lead precipitates produced in the direct preparation of frangulic acid from rhamnus bark by extraction with dilute soda-lye. It has a strong resemblance to frangulic acid, but is of a darker colour. It melts at  $248^\circ$ – $250^\circ$ . This agreement in the melting-points is probably due to the circumstance that frangulic acid, when melting, or immediately previously, is converted into difrangulic acid by elimination of water. Kubly's aromin is also probably identical with frangulin, and aromic acid with frangulic or difrangulic acid.

*Trioxyanthraquinons*,  $C_{14}H_5(OH)_3O_2$ .

In the trioxyanthraquinons, three hydrogen atoms of anthraquinon are replaced by hydroxyl, according to the posi-

tion of which several isomers may exist, some of which are actually known. All the trioxyanthraquinons known are true dyes, which speaks in favour of the influence of the position of the hydroxyls in the benzol nuclei, since in the trioxyanthraquinons at least 2 OH groups must be present in one of the benzol nuclei. The trioxyanthraquinons have not been obtained synthetically, and the preparation of the individual members of this group, as well as the relative position of the hydroxyls, in as far as hitherto known, was described under the purpurins in question.



The history of purpurin is closely connected with that of alizarin, though it has been much less abundantly studied. It received its name from Robiquet and Colin, who discovered it simultaneously with alizarin, but who did not obtain it perfectly pure. Like alizarin, it was described under a variety of synonyms: Gaultier, De Claubry, and Persoz named it 'matière colorante rose'; Runge called it madder-purple, and Debus oxylicaric acid. The latter proposed the formula  $\text{C}_{30}\text{H}_{10}\text{O}_{10}$  ( $\text{C}=6$  and  $\text{O}=8$ ), whilst Rochleder preferred  $\text{C}_{60}\text{H}_{20}\text{O}_{20}$ , and Schiel  $\text{C}_{25}\text{H}_{16}\text{O}_{16}$ . Wolff and Strecker assigned it the formula  $\text{C}_{15}\text{H}_6\text{O}_8$ , which agrees well with the results obtained by Debus. This view was generally adopted for some time. Quite recently, however, since purpurin, owing to Kopp's method of separation, was found in commerce tolerably pure, it was re-examined.

Schützenberger and Schiffert obtained very accordant results in a series of investigations, from which they deduced the formula  $\text{C}_{20}\text{H}_{12}\text{O}_7$  ( $\text{C}=12$ ). Their results agree, however, better, and indeed somewhat decidedly with the formula  $\text{C}_{14}\text{H}_8\text{O}_5$ , as Strecker pointed out on publishing his analyses of alizarin.



That this formula is correct appears from the observations of Graebe and Liebermann, that purpurin as well as alizarin yields anthracen on heating with zinc-powder.

Purpurin, like alizarin, must be regarded as a quinon; it is oxyalizarin, or trioxyanthraquinon,  $C_{14}H_8(OH)_3(O)_2''$ .

In purpurin the three hydroxyls exist in one benzol nucleus, which is proved by the fact that purpurin, on oxidation with nitric acid, yields phthalic and oxalic acids like alizarin. This view is also supported by De Lalande's synthesis of purpurin from alizarin, also its preparation from quinizarin, discovered by Ad. Baeyer and Caro. As the hydroxyls in alizarin take the position 1·2, and in quinizarin 1·4, the third hydroxyl, entering in the formation of purpurin, must have either the positions 1·2·4 or 1·3·4, which,

as the adjacent position of the group of carbon atoms  $\begin{array}{l} -CO- \\ -CO- \end{array}$

presupposes, are identical. The formation of purpuroxanthin is also in favour of the accuracy of this assumption. Like alizarin, purpurin is present in madder, not in the free state, but as a glucoside, which has not yet been isolated, as it is very easily resolved into purpurin and sugar, and is far less stable than ruberythric acid, as will appear from the separation of alizarin and purpurin on Kopp's method.

The isolation of purpurin from alizarin, except by Kopp's method, depends on the solubility of the former in alum-water, in which alizarin is only somewhat soluble at the boiling-point, and is deposited on cooling.

Robiquet and Colin treat ground madder, previously washed in water, with concentrated sulphuric acid, and extract the black residue with boiling alum-water. The purpurin dissolves, and is reprecipitated by sulphuric acid, collected, washed, dried, dissolved in ether, and obtained on evaporation as crystals in a purified state, though still containing a little alizarin.

It is better, as Runge directs, to let the decoction of

madder in alum-water cool, remove the deposit of alizarin, add dilute sulphuric acid, collect the precipitate, and wash first with pure, and then with acidulated water, dry, dissolve in alcohol at 80–90 per cent., evaporate till crystalline crusts are deposited, redissolve in boiling alcohol, recrystallise, and finally dissolve in ether, obtaining the purpurin in crystals on evaporation.

Debus prepares purpurin in a similar manner. He extracts madder-root in 15 to 20 parts of boiling water, filters, boils the decoction for some time with lead oxide in excess, filters, washes the precipitate on the filter with water, decomposes it with dilute sulphuric acid, and extracts the liberated colouring-matter from the sulphate of lead by boiling with alcohol. The alcoholic solution is agitated by calcined oxide of zinc as long as this takes a red colour. He then filters the zinc compound, washes with alcohol, and decomposes with dilute sulphuric acid. The colouring-matters liberated are dissolved in ether, again precipitated with zinc oxide, and the zinc compound decomposed with sulphuric acid. The washed colouring-matters are then boiled with strong alum-water till the solutions cease to deposit anything on prolonged standing. The body deposited is alizarin.

The dark-red aluminous solutions are decomposed with dilute sulphuric acid, when purpurin is deposited after standing from twelve to twenty-four hours. This is boiled with dilute sulphuric acid in order to remove traces of alumina, washed in water, and dissolved in 150–200 parts of alcohol with the aid of heat.

In the course of two or three hours the colouring-matter is deposited in red needles from two or three lines in length; these are purified by recrystallisation.

According to E. Kopp's method, madder is extracted with aqueous sulphurous acid; about 3 to 5 per cent. of sulphuric or hydrochloric acid is added to the liquid, and the whole is

heated to  $50^{\circ}$  or  $60^{\circ}$  C., when the purpurin is deposited in flocks. If this temperature is not exceeded, the precipitation of the flocks is completed in twenty to thirty minutes. Sometimes these flocks contract, become heavy and granular, and separate as a more or less pulverulent mass, which has a finer red colour the denser it is. The mass is washed with a little cold water, till it runs off with a yellow, or only faint red colour, and has no longer an acid reaction. We thus obtain purpurin in larger or smaller fragments, and almost chemically pure. It is obtained in a state of absolute purity by repeated crystallisation from alcohol.

It has not yet been found possible to obtain purpurin from alizarin by means of the sulpho-acids, as the bisulpho-acids, from which it should be formed, contain the sulphuric acid residues distributed in both benzol-groups. On the other hand, F. De Lalande succeeded in obtaining purpurin from alizarin by the following method:—To 8–10 parts of concentrated sulphuric acid is added 1 part of dry powdered alizarin and 1 part of dry arsenic acid, or peroxide of manganese. The temperature is gradually raised to  $150^{\circ}$ – $160^{\circ}$ , till a drop of the mixture thrown into slightly alkaline water takes the red colour of purpurin. The mass is then treated with much water, the precipitate washed with cold water, dissolved in a sufficiency of saturated alum-water, and reprecipitated by the addition of an acid. It is completely purified by repeated treatment with alum, and recrystallisation from superheated water. Rosenstiehl, who repeated De Lalande's process, confirms his account. Baeyer and Caro have also obtained purpurin from quinizarin by the same method. They heated the latter compound to about  $140^{\circ}$  with sulphuric acid and manganese. It is remarkable that whilst all three bioxyquinons which contain the two hydroxyls in the same benzol nucleus yield the same purpurin, one only gives purpuroxanthin on its reduction. Rosenstiehl obtained purpurin from pseudopurpurin by boiling with alcohol at

20 per cent., or with boiling water. It will be seen here that the alcohol and the water effect a true reduction, which, especially in the case of water, can only occur at the expense of a part of the pseudopurpurin. This reaction, however, goes further; there is always and simultaneously formed a small quantity of purpuroxanthin. This action may take place at a temperature below  $100^{\circ}$ , if we use crude pseudopurpurin or madder (previously washed) in presence of acidulated water, or an aqueous solution of alum, which is a good solvent of this substance. In this case some one of the constituents of madder probably occasions the reaction. Schützenberger and Schiffert obtain purpurin from pseudopurpurin on heating to  $200^{\circ}$  with alcohol or by sublimation. It was formerly supposed that purpurin, in its ordinary state, did not dye fast shades, but obtained permanence only on heating or sublimation. The purpurin of commerce was, therefore, mixed with glycerin, and the mixture heated to  $112^{\circ}$ – $120^{\circ}$ . A conversion of pseudopurpurin into purpurin would here certainly occur. If commercial purpurin is heated under pressure to  $120^{\circ}$  along with hydrochloric acid, the mass, originally red and amorphous, is converted into a garnet-red crystalline substance, which well assists the action of soap.

Purpurin dyes tissues mordanted with alumina scarlet to dark-red. On soaping, the colour becomes scarlet. Cotton, prepared for Turkey-reds with oil mordant, is dyed a brown-red by purpurin; but after treatment with soap and soda, it becomes a fiery Turkey-red. Purpurin dyes readily with mordants in distilled water. The addition of a quantity of dissolved carbonate of lime, corresponding to a lake, with 1 atom of calcium, is not injurious; but a larger addition of lime causes the formation of an insoluble lake, with 3 atoms of calcium, which does not dye, and which is very slowly decomposed by carbonic acid.

In America, purpurin is said to be used in dyeing along

with anilin colours. The goods are probably grounded with purpurin, and topped with anilin colours.

Purpurin has a more intense red colour than alizarin. It sublimes at  $250^{\circ}$  with partial decomposition, leaving a shining carbonaceous residue. The crystals are found in plumose groups.

Sublimed purpurin crystallises from alcohol in fine-red, slightly orange needles, often a centimetre in length. Unsublimed purpurin in the same circumstances forms only very small needles.

In water it is rather more soluble than alizarin. It is more freely soluble in ether, alcohol, benzol, glycerin, concentrated sulphuric acid, and acetic acid. Nitric acid oxidises it to phthalic and oxalic acids. If heated with zinc-powder, it yields anthracen. In alkalis it dissolves with a purple-red colour. The soda-salt is readily obtained in crystals, if an alcoholic solution of soda is mixed with an alcoholic solution of purpurin, and a little ether is added. It is then deposited in fine needles.

Alkaline carbonates, indeed all alkaline compounds with a basic reaction, dissolve it with a red colour. In alum-water it is much more soluble than alizarin, and purpurin is not deposited from saturated and hot solutions on cooling. Hydrate of soda at a boiling heat withdraws purpurin from its alumina-lake. Purpurin may be readily distinguished from alizarin by the colour of its compounds with alkalis. The alkaline solutions of alizarin are violet, but those of purpurin a fine purple-red.

*Purpuramid, or Purpurein*,  $C_{14}H_5NH_2(OH)_2O_2$ .

Purpurin dissolves in ammonia with a fine-red colour, and is precipitated unchanged on the addition of acids. But if the solution is allowed to stand twenty-four hours, or heated to a boil, acids no longer precipitate purpurin, but purpuramid, in

reddish-violet flocks. Purpuramid is, therefore, more easily produced than alizaramid. Purpuramid dissolves in soda-lye with a red colour, and with escape of ammonia. In boiling alcohol it dissolves with a red-violet colour, and forms, on evaporation of the alcohol, crystals almost black, with a green surface reflection, resembling those of murexide.

It dyes wool and silk an amaranth-red without mordant.



Obtained by heating crystallised purpurin-soda with iodide of ethyl to 150° C. in sealed tubes.

On the addition of alcohol, iodide of sodium separates out, along with red crystalline grains of triethylpurpurin, sparingly soluble in alcohol. The salts of purpurin have been but little examined. The following are the colours of some precipitates produced by reagents in alkaline solutions of purpurin :—

|                              |                |
|------------------------------|----------------|
| Chloride of barium . . . .   | Red.           |
| Chloride of calcium . . . .  | Red.           |
| Acetate of lead . . . .      | Red.           |
| Ferric chloride . . . .      | Red-brown.     |
| (Soluble in much water).     |                |
| Sulphate of magnesia . . . . | Red.           |
| Nitrate of silver . . . .    | Red.           |
| (Red-brown on heating).      |                |
| Mercurous chloride . . . .   | Red-brown.     |
| Stannic chloride . . . .     | Yellowish red. |

The changes produced in purpurin by reducing agents have been already examined by Bolley and Rosa, and by Schützenberger, without any certainty having been reached. Latterly, however, purpuroxanthin, a reduction-product, identical with Schützenberger's xanthopurpurin, has been accurately described.

*Hydrate of Purpurin.*

This compound was described by Schützenberger as orange colouring matter, and is found in commercial purpurin, from which it has been recently obtained by Rosenstiehl. According to Schützenberger, the hydrate is obtained from commercial purpurin as follows: The purpurin is treated with 85 per cent. alcohol and filtered. On cooling, some fine needles of impure purpurin separate. These are removed by filtration and the filtrate is concentrated by evaporation. When cold, the filtrate becomes a curdy crystalline mass, which is pressed, redissolved in luke-warm alcohol, and on crystallisation yields the orange colouring-matter in a very pure condition. More of this orange colour is obtained when the mother-liquors from the pressed curd-like mass are evaporated to dryness and the residue is treated with rectified benzol. This leaves the orange colouring-matter undissolved, whilst it takes up the yellow principle, xanthopurpurin or purpuroxanthin.

According to Rosenstiehl, the hydrate is obtained on precipitating a solution of purpurin in alkali or in alum-water with an acid.

The hydrate of purpurin is insoluble in boiling benzol, very readily soluble in luke-warm alcohol. It is deposited from a concentrated alcoholic solution either in small orange leaflets or in a curdy greenish crystalline mass. Heat converts it into purpurin. With calcareous water it behaves like purpurin. The shades which it dyes resemble those of purpurin after the latter have been soaped. It appears as if purpurin is converted into the hydrate upon the tissue. The rose shades produced by purpurin and its hydrate are equally fast, and are obtained in the same manner as an alizarin-rose, but they do not resist the action of the sun equally well.

*Isopurpurin*,  $\text{C}_6\text{H}_3(\text{HO})\text{C}_2\text{O}_2 \cdot \text{C}_6\text{H}_2(\text{OH})_2$ .

This isomer of purpurin was discovered by Auerbach in a product manufactured by Gessert Brothers under the name 'artificial purpurin,' and subsequently described by Perkin as anthrapurpurin. Perkin's anthrapurpurin was said to be distinguished from Auerbach's isopurpurin by its insolubility in alcohol, and by the sparing solubility of its soda-salt in the same solvent. Subsequent researches, however, have proved the identity of both compounds. Its preparation from the crude product, however, is very tedious, and it is better to obtain isopurpurin from bisulphanthraquinonic acid. If  $\beta$ -bisulphoanthraquinonic acid is heated with caustic soda, the first product of the reaction is bisulphoxyanthraquinonic acid, which dissolves in alkalis with a red colour, then isoanthraflavic acid, and lastly isopurpurin. In isopurpurin, as in isoanthraflavic acid, the three hydroxyls are distributed in both benzol nuclei, so that one is present in the one and two in the other. This is proved by the fact that isopurpurin, on oxidation with nitric acid, yields no phthalic acid. It is not yet decided how the hydroxyls are placed. Isopurpurin crystallises in orange anhydrous needles, and is very soluble in boiling alcohol. In boiling water it is somewhat soluble, and on continued boiling the solution takes a red colour. It dissolves sparingly in ether, but readily in glacial acetic acid, whence it separates on cooling in crystals arranged in stellar groups. In concentrated sulphuric acid and in potassa-lye it dissolves with a red-violet colour, the tone being redder than that of an alkaline solution of alizarin. In hot baryta-water it dissolves with a violet colour. The solution in carbonate of soda is red, with a decided brown cast. In boiling alum-water it is very sparingly soluble. The solution is reddish-yellow and the isopurpurin is chiefly redeposited on cooling. In ammonia it dissolves with a violet colour. With alcoholic



acetate of lead it gives a purple precipitate, which dissolves with a violet colour on boiling with an excess of the precipitant. Alcoholic copper-acetate gives a fine violet solution.

The alkaline alcoholic solution shows the absorption-bands having the same position as those in alizarin. It sublimes in orange needles, and with mordants dyes shades between those of alizarin and natural purpurin. Its melting-point is above  $360^{\circ}$ .

Like alizarin, isopurpurin forms acetyl- and benzyl-compounds, which have been obtained and described by Perkin. Triacetylisopurpurin,  $C_{14}H_5(C_2H_3O)_3O_2$ , crystallises in pale-yellow scales and melts at  $220^{\circ}$ – $222^{\circ}$ .

*Flavopurpurin*,  $C_{14}H_5O_5$ .

Flavopurpurin is obtained from  $\alpha$ -bisulphanthraquinonic acid in the same manner as isopurpurin from the  $\beta$ -acid, from the first product of the reaction, anthraflavic acid. In flavopurpurin the two hydroxyls are distributed between both benzol nuclei, as anthraflavic acid is formed from metaoxybenzoic acid. Like isopurpurin, flavopurpurin can be obtained from the red alizarin of commerce. Its preparation in this manner is very tedious, as flavopurpurin agrees very closely in its properties with isopurpurin, and can only with difficulty be separated from the latter. It is best to make use of  $\alpha$ -bisulphoanthraquinonate of soda, which in its external appearance resembles the monosulphanthraquinonate.

Flavopurpurin crystallises in anhydrous yellow needles, sparingly soluble in boiling water but readily in cold alcohol. The aqueous solution remains yellow on boiling. It is sparingly soluble in ether, but dissolves in boiling glacial acetic acid, from which it separates on cooling in stellar crystals. In concentrated sulphuric acid it dissolves with a red-brown colour, and in potassa-lye with a purple, redder

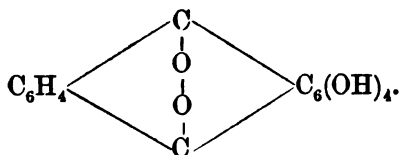
than anthrapurpurin. On dilution, or on the addition of a little dilute alkali, the solution appears of a pure red. The colour disappears on prolonged standing. In hot baryta-water it is sparingly soluble with a reddish-violet colour. The solution in deep layers displays absorption-bands. In ammonia it dissolves with a yellowish-red colour and shows no bands. It dissolves in carbonate of soda with a yellowish-red colour. Alcoholic lead acetate gives a reddish-brown precipitate very sparingly soluble in excess with a red colour. Alcoholic copper acetate gives a red solution; in alum it is sparingly soluble. The melting-point of flavopurpurin is above  $330^{\circ}$ . It sublimes in long needles resembling alizarin, and dyes with mordants. The tones produced, however, are much yellower than those of purpurin and isopurpurin. The alkaline solution shows likewise two bands, rather more distant from the red, and a broad stripe in the blue.

*Oxychryszazin*,  $C_{14}H_8O_6$ .

Obtained by Liebermann and Giessel on melting chryszazin with alkali. On melting, the original red colour of the solution of chryszazin passes into a 'corn-flower' blue coloured mass of a splendid metallic lustre. The solution of this substance appears of a blue violet, almost like that of alizarin. Acids precipitate the colouring-matter in brown flocks, which can be recrystallised from alcohol. From its solution in carbonate of soda, it is almost entirely precipitated by alumina. With mordants it dyes intense shades, the colours being intermediate between those of alizarin and purpurin.

*Tetraoxyanthraquinon*,  $C_{14}H_4(OH)_4O_2$ .

Three isomers of this oxyanthraquinon are known; but as there can exist only one containing four hydroxyls in one benzol-nucleus, in the others the hydroxyls must necessarily be distributed in both.

*Pseudopurpurin,*

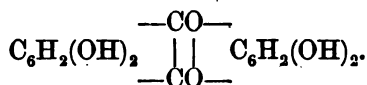
This compound, discovered by Schützenberger and Schiffert, constitutes about three-fourths of the bulk of artificial purpurin. The discoverers proposed the formula  $\text{C}_{20}\text{H}_{12}\text{O}_9$ ; but Graebe and Liebermann already expressed the view that, as a derivative of anthraquinon, it must have the formula  $\text{C}_{14}\text{H}_8\text{O}_6$ , an opinion which has been confirmed by subsequent researches. As pseudopurpurin yields on oxidation phthalic acid, the four hydroxyls must be contained in one benzol-nucleus, which is supported by the reduction to purpurin and purpuroxanthin.

To obtain pseudopurpurin, crude purpurin, preferably obtained according to E. Kopp's method, is treated with luke-warm alcohol at 85 per cent. The solution, which contains purpuroxanthin and the hydrate of purpurin, is filtered off, and the residue, which forms about nine-tenths of the whole mass, is extracted with strong boiling alcohol and filtered. The filtrate, on cooling, deposits purpurin in fine needles, almost pure. The mass remaining after the extraction with alcohol is a red powder. It is dried, and repeatedly boiled with benzol, the orange solution being filtered whilst hot. On cooling, it quickly solidifies to a crystalline paste, which is pressed. The crystals from the first benzol extracts consist of purpurin, but those from the latter crystallisations are almost entirely pseudopurpurin. Pseudopurpurin is almost insoluble in boiling alcohol, soluble in boiling benzol, from which it is almost entirely redeposited on cooling, forming a crystalline paste of fine needles which, when dry, have a brick-red colour. On heat-

ing, it is decomposed with formation of purpurin. It undergoes the same decomposition if heated to  $200^{\circ}$  with alcohol. It dissolves readily in alkalis with a red colour. With ammonia it forms an amido-derivative resembling purpuramid.

Pseudopurpurin dyes only in distilled water. A quantity of carbonate of lime corresponding to a lake with 1 atom of calcium, converts it entirely into an insoluble compound which is not decomposed by carbonic acid. With aluminous mordants, it dyes shades approaching those given by alizarin. With iron mordants it dyes a violet grey (5 violet-blue three-tenths or four-tenths). The colours are distinguished from those produced by the remaining madder-fragments because a passage through the soap-beck, far from brightening, quickly destroys them. Pseudopurpurin therefore plays no part in dyeing, both on account of the readiness with which it forms an insoluble lime-compound and on account of its slight power of resistance to the agents required in clearing. It is only useful by reason of its conversion into purpurin. Still it has received an industrial application, as it forms the colouring-matter of madder-lake, which yields so bright a rose, and which was in use long before the discovery of alizarin.

*Anthrachryson,*



This compound is formed on heating dioxybenzoic acid with 4 parts of sulphuric acid to  $140^{\circ}$ . According to its formation, it contains two hydroxyls in each benzol nucleus. It crystallises from alcohol in fine yellowish-red needles, which melt at  $320^{\circ}$ , and are very insoluble in water, sparingly soluble in alcohol and ether. Alkaline lyes dissolve with a red colour.

*Rufiopin*,  $C_{14}H_8O_6$ .

This colouring matter was obtained by Liebermann and Chojnacki by the action of sulphuric acid upon opianic acid. To obtain it, opianic acid is heated with 30 parts of concentrated sulphuric acid to  $180^\circ$  in the sand-bath, the liquid taking a violet colour. When cold, it is poured into water, which precipitates the colour in black flocks. By repeatedly dissolving the precipitate in soda-lye, filtration, and precipitation with acid, it is obtained of a yellowish-brown colour. By crystallisation from ether, it is obtained in yellowish-red crusts, which are perfectly freed from foreign matter by a repetition of the whole process of purification.

If distilled with zinc-powder, it yields anthracen. In potassa it dissolves with the colour of purpurin; but from this compound and from alizarin it is distinguished by the violet-red colour of its solution in concentrated sulphuric acid, which completely resembles that of rufigallic acid. The latter, however, dissolves in potassa with a blue colour, and is rapidly deposited on exposure to the air, which is not the case with rufiopin. With solutions of lead and baryta, rufiopin yields precipitates.

With mordants, it dyes shades which resemble those of rufigallic acid, rather than of alizarin.

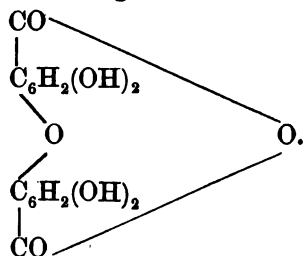
*Rufigallic Acid*,  $C_{14}H_8O_8$ .

Obtained first by Robiquet on treating gallic acid with four parts of concentrated sulphuric acid at  $140^\circ$ . He considered that rufigallic acid was formed from gallic acid by the separation of water, according to the formula  $C_7H_6O_5 - H_2O = C_7H_4O_4$ .

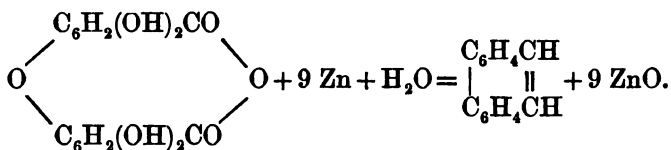
Löwe rejected this formula, depending upon the evolution of sulphurous and carbonic acids observed during its formation, which, however, are probably due merely to a further

decomposition of a part of the gallic acid. He proposed the formula  $C_{10}H_6O_6$ . Jaffé, who succeeded in forming anthracen by the reduction of rufigallic acid, preferred the formula  $C_{14}H_8O_8$ , doubling Robiquet's original numbers.

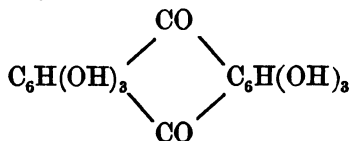
Lauth and Grimaux disputed this formula, and Schiff, who regarded it as an acid and ethereal anhydrid of gallic acid, assigns it the following constitution:—



As an especial confirmation of this formula, Schiff refers to the replacement of 4 hydroxyls by acetyl; whilst according to Jaffé's formula 6 hydroxyls should be capable of replacement. According to Schiff's formula, the origin of anthracen cannot be explained. Were it correct, the reaction ought to have produced, not anthracen, but phenanthren,

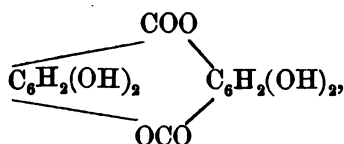


Klobukowsky and Nölting repeated Jaffé's experiment, and confirmed it; they obtained a hydrocarbon possessing all the properties of anthracen, and they finally succeeded in obtaining an acetyl-compound, which, being analysed, indicated 6 acetyl-groups. If, therefore, the formula

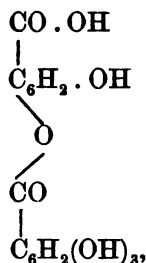


is not demonstrated, it is rendered highly probable

Besides the formula of anthraquinon, a compound of two molecules of gallic acid, with separation of 2 H<sub>2</sub>O, is conceivable, according to the following formula :—



which explains the formation of anthracen. Independently of the consideration that this formula of Schiff's is rightly attributed to ellagic acid, it is inadmissible, as otherwise tannic acid,



would yield rufigallic acid more readily than gallic acid, whilst in fact the former gives mere traces. According to this formula also, tannic acid with zinc-dust should also yield anthracen, which is not the case. The anthraquinon formula is further supported by the reduction of rufigallic acid with hydriodic acid. If rufigallic acid is heated with hydriodic acid and phosphorus, anthracen is not indeed formed directly; but there appears a substance, which crystallises in microscopic yellow needles, and which, if distilled with zinc-dust, yields anthracen, but differs in its properties from all known derivatives of anthracen. (Probably this compound is a substance similar to purpuroxanthin, and formed from purpurin and pseudopurpurin by reduction.)

According to Wagner, rufigallic acid is obtained as

follows: 1 part of gallic acid is slowly heated to  $140^{\circ}\text{C}$ . with 4 parts of concentrated sulphuric acid. Löwe, however, has shown that the conversion of gallic acid into the rufigallic is complete even at the temperature of the water-bath. The red solution, when cold, is poured into water, when a red-brown precipitate is formed, partly flocculent, and partly granular crystalline, and is freed from adherent sulphuric acid by decantation, and finally by washing on the filter.

The small shining crystals obtained by elutriation lose their crystalline water at  $120^{\circ}$ . If more strongly heated, rufigallic acid sublimes in vermilion prisms. It is insoluble in cold water, sparingly soluble at  $100^{\circ}$ , sparingly soluble in boiling alcohol and ether, insoluble in oil of turpentine and chloroform, but in acetone it dissolves with a brown colour. Alkalis dissolve it with a brown colour if air is excluded, but if the air has access, humus-like bodies are formed. If covered with ammonia, it takes a red colour. Baryta converts it into an indigo-blue mass, without solution. If introduced into melting potassa, it becomes a splendid green, and then turns indigo-blue in places. On the addition of water it turns indigo-blue, and is decomposed with the formation of oxyquinon,  $\text{C}_6\text{H}_4\text{O}_3$ . On treatment with zinc-powder, anthracen is formed, just as is the case with alizarin. If treated with reducing agents, reduction-products are formed; but alizarin has not yet been obtained by this process. Tissues mordanted with salts of alumina and iron are dyed by rufigallic acids, in shades resembling those of alizarin, but duller and dirty. They resist soaping, however, perfectly.

The first experiments on the tinctorial properties of rufigallic acid were made by Robiquet.

*Chrysophanic Acid*,  $\text{C}_{16}\text{H}_{10}\text{O}_4$ .

This acid, though not a direct derivative of anthracen, is interesting, on account of its derivation from methylanthra-



ceu, and may therefore be appropriately considered here, along with its congener, emodin.

In their earlier papers, Graebe and Liebermann ascribed to chrysophanic acid the formula  $C_{14}H_8O_4$ , and regarded it as an isomer of alizarin. They were led to this view because chrysophanic acid, on reduction with zinc-powder, produces a hydrocarbon very similar to anthracen, and because, on analysing the acid, they obtained figures closely approximating on those required by alizarin. In their subsequent researches on emodin, Liebermann and Fischer ascertained the connection of the two compounds, and subjected chrysophanic acid to a re-examination. The result was that chrysophanic acid is a derivative of methylanthracen, and bears to emodin the same relation as does purpurin to alizarin. They proved that the hydrocarbon obtained, on its reduction with zinc-powder, was methylanthracen, by converting it into anthraquinoncarbonic acid and methylanthraquinon.

The acid occurs in the roots of various rhubarbs and docks, as *Rumex obtusifolius*, *patientia*, *palustris*, &c., in the lichen *Parmelia paricina*, in senna-leaves, &c. It was formerly obtained in an impure state from these sources; and, according to its origin, was named rhein, rhubarb yellow, phaeoretin, erythrosetin, rhaponticin, rumicin, lapathin, parietin, &c. For its preparation various methods have been proposed. Rochleder extracts the rhubarb or the lichens with very weak alcohol, to which a little potassa-lye has been added, filters, presses the residue, and passes a current of carbonic acid through the liquid. The precipitate is filtered, dissolved in alcohol at 50° per cent., mixed with a little potassa-lye, filtered, and the filtrate precipitated with acetic acid. The precipitate is collected, dissolved in boiling alcohol, and filtered whilst hot. The filtrate is mixed with water, and the acid thus separated is obtained pure on recrystallisation from alcohol.

Warren De la Rue extracts rhubarb with benzol, distills off the benzol, and, when most of it has gone over, allows the residue to cool. Impure chrysophanic acid crystallises out, and is redissolved in boiling benzol, filtered, crystallised on cooling, and purified by solution in glacial acetic acid.

Batka treats rhubarb or senna-leaves with caustic-potassa, filters, and precipitates chrysophanic acid from the filtrate by the addition of hydrochloric acid. The precipitate is washed on the filter, well dried, extracted with chloroform, and evaporated. Chrysophanic acid remains in the capsule as fine-yellow granular crystals.

Chrysophanic acid either forms gold-coloured crystals, or orange-red masses of a golden lustre, like crystalline iodide of lead. From benzol it crystallises in hexagonal monoclinar tables, of a yellow or orange colour; from glacial acetic acid, alcohol, and fusel oil, it is deposited in mossy aggregation. It is inodorous and almost tasteless, scarcely soluble in cold, and very slightly in hot water. In cold ether and alcohol it dissolves with a yellow colour. One part of chrysophanic acid dissolves in 224 parts of boiling alcohol at 86 per cent., or in 1125 of alcohol at 30 per cent. In aqueous alkalis it is sparingly soluble with a red colour. Acids turn the red solutions yellow. The alkaline solution can be evaporated to dryness without decomposition, but at a certain stage of concentration the soda-salt is separated out in blue flocks, with a violet cast.

Chrysophanic acid melts, without decomposition, at 162°, and crystallises on cooling. At higher temperatures a portion of the acid is decomposed, but another portion sublimes in golden-yellow needles. It dissolves, without decomposition, in concentrated sulphuric acid and dilute nitric acid; concentrated nitric acid at a boiling heat converts it into chrysammic acid. Potassa-lye has scarcely any decomposing action. According to Warren De la Rue, the red alkaline solution of chrysophanic acid turns blue on con-

centration. The blue compound turns red on solution in water, and on mixture with hydrochloric acid chrysophanic acid is deposited undecomposed. On prolonged melting with hydrate of potassa, chrysophanic acid is decomposed, and a strongly fluorescent compound is formed. The ammonia-compound is decomposed on boiling in water, and undecomposed chrysophanic acid is left behind. Phosphorus perchloride forms a chlorine-compound, which, on heating with water, forms chrysophanic acid again.

It is a very feeble acid. The alkaline-salts are blue or violet, and are deposited in blue flocks on concentrating the aqueous solutions. The lime- and baryta-salts are obtained by mixing an alkaline solution of chrysophanic acid with chloride of calcium or of barium. They are insoluble in water, and are readily decomposed in the air by absorbing carbonic acid. If a solution of chrysophanic acid is mixed with an alcoholic solution of basic acetate of lead, there is formed a slight whitish precipitate, which disappears on boiling. Subsequently carmine-red flocks are deposited, which are insoluble in water, and are decomposed by alcohol.

*Acetylchrysophanic Acid*,  $C_{15}H_8O_2(O.C_2H_3O)_2$ .

This compound is obtained by heating chrysophanic acid and acetyl chloride in sealed tubes in the water-bath. It separates out in pale yellow crystals, which are soluble in dilute alcohol, but soon decomposed into chrysophanic and acetic acids.

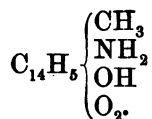
*Benzoylchrysophanic Acid*,  $C_{15}H_8O_2(O.C_7H_5O)_2$ .

Obtained by introducing chrysophanic acid into chlorobenzyl heated almost to a boil. The resulting crystalline mass is pressed, and forms coloured crystals of a silky lustre. In alcohol it is sparingly soluble, more freely in benzol, from which it crystallises in long irregular

hexagonal prisms. At 200° it melts to a dark-yellow liquid, which congeals again on cooling and gives off yellow vapours at higher temperatures. Ammonia and aqueous potassa do not act upon it, but it is immediately decomposed by alcoholic potassa. The latter, as also concentrated sulphuric acid, resolves it into benzoic and chrysophanic acids.

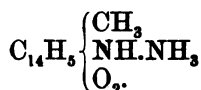
*Amides of Chrysophanic Acid.*

These compounds were obtained by Liebermann and Fischer on heating chrysophanic acid and ammonia in sealed tubes. At 200° a part of the substance is carbonised, but the principal product is chrysophanamid; at 150° there occurs no carbonisation, but along with chrysophanamid there is formed in predominating quantity a second compound, which separates from the solution in long dark needles. To obtain chrysophanamid, the contents of the tube after heating to 180°–200° are filtered and precipitated with an acid, but complete solution only takes place on prolonged standing. The precipitate filtered off is heated for some time with alcohol, acidulated with hydrochloric acid, and precipitated with water. It is freed from undecomposed or from re-formed chrysophanic acid by means of cold baryta-water, when the amid dissolves as a barium-salt of a red colour, whilst chrysophanate of barium remains undissolved. The yellowish brown flocks of the amid precipitated from the filtrate by an acid appear after recrystallisation from alcohol as small indistinct yellow scales, of the composition

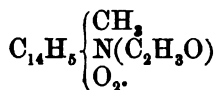


On boiling with baryta-water, alkalis, or dilute acids, the amid is converted into chrysophanic acid, with escape of ammonia.

If aqueous ammonia acts upon chrysophanic acid at 150° as above mentioned, there is formed along with the amid a compound which is deposited in the tube in crystals of a metallic lustre. After being washed with very dilute ammonia, this substance is triturated with hydrochloric acid and dissolved in cold baryta-water to remove chrysophanic acid, and reprecipitated with an acid. The yellow flocks, on washing with water, change their colour to an intense brick-red, an indication of the transient formation of an unstable compound with acid. The substance is an ammonia-compound of chrysophanimid.



The free imid cannot be obtained from it, since, if it is treated with alkalis or acids in order to remove ammonia, it takes up water and passes first into chrysophanamid and ultimately into free chrysophanic acid. It is, however, easy to obtain an acetylated imid from the ammonia-compound of the imid with anhydrous acetic acid by boiling in a flask fitted with a cohobater. It separates as a dark-green powder, soluble scarcely in a trace in the ordinary solvents. Chloroform dissolves very small quantities; the substance sometimes separates from the grass-green solution in beautiful needles of a violet metallic lustre. Analysis leads to the formula



Soda-lye does not decompose the compound; concentrated sulphuric acid dissolves it with a brownish-yellow colour, and decomposes it with the aid of heat, forming chrysophanic acid. The behaviour of nitric acid is similar.

*Emodin*,  $C_{15}H_{10}O_5$ .

This compound accompanies chrysophanic acid, and is found in rhubarb root to the extent of about 2 per cent. of the latter. It bears to chrysophanic acid a relation similar to that of purpurin to alizarin, i.e., it is a trioxymethyl-anthraquinon, whilst chrysophanic acid is a dioxymethyl-anthraquinon. De la Rue and Müller, as also Rochleder, obtained on the analysis of emodin tolerably concordant numbers, and proposed at first the formula  $C_{40}H_{30}O_{13}$ . Skraup, who examined it, subsequently adopted the formula  $C_{32}H_{24}O_{11}$ . Liebermann, on reducing emodin with zinc-powder, obtained a compound resembling anthracen, but his analyses led to the formula  $C_{15}H_{10}O_5$ , and thus, as well as by the proof that the product of the reaction with zinc-powder is methylantracen, the connection between that body and emodin was established.

To obtain it, crude chrysophanic acid is boiled with soda-lye and filtered whilst boiling. Chrysophanic acid remains almost entirely undissolved, whilst all the emodin is taken up with a blood-red colour, and is precipitated by acids from this solution in amorphous yellow flocks, which are purified by recrystallisation from boiling alcohol at about 80 per cent. The colour of emodin is not so light a yellow as that of chrysophanic acid, but inclines to orange.



## APPENDIX.

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### MONOSULPHOANTHRACENIC ACIDS AND ANTHROLS.

These bodies were obtained by E. Lincke on heating 1 part of anthracen with 3 parts of concentrated sulphuric acid. There are formed two isomeric monosulpho-acids, which may be separated by means of their lead-salts, and  $\alpha$ -monosulphanthracenic acid,  $C_{14}H_9SO_3H$ , forms yellowish columns or tables. It is somewhat soluble in hot water but not very much more than in cold. It is stable in the air. Its lead-salt  $(C_{14}H_9SO_3)_2Pb + 4 H_2O$  crystallises in light-yellow leaflets, dissolves very readily in hot water, rather less freely in cold. The barium-salt, with  $6 H_2O$ , forms yellowish needles, and dissolves in water still more easily than the lead-salt. The sodium-salt crystallises in microscopic plates; it is very soluble in water, and, like the lead-salt, rather more freely with the aid of heat than in the cold.

#### *$\beta$ -Monosulphanthracenic Acid, $C_{14}H_9SO_3H$ .*

It forms long beautiful light-yellow columns, and is very sparingly soluble in water, even when boiling. The barium-salt, with  $7 H_2O$ , is somewhat more soluble than the lime-salt, and separates from the hot saturated aqueous solution in beautiful nacreous tables of a faint-yellowish colour. The sodium-salt crystallises in fine long yellowish columns, and is sparingly soluble, though more freely in hot than in cold water.

From the potash-salts of these acids two anthrols are obtained by melting with hydrate of potassa :— $\alpha$ -anthrol,  $C_{14}H_9OH$ . It crystallises in brilliant light-yellow needles, sometimes in leaflets, easily soluble in ether, alcohol, and benzol, less readily in chloroform, but insoluble in water. In alkalis it dissolves readily, and, if air be absent, is precipitated unchanged by acids. In alkaline solutions, if boiled in water with access of air, it is oxidised to a dark-brown



substance. At  $250^{\circ}$  it is decomposed without previous fusion. With bromine it gives a flocculent product, and with concentrated sulphuric acid it forms a sulpho-acid.  $\beta$ -anthrol,  $C_{14}H_9OH$ , forms yellowish columns, and is rather more sparingly soluble in ether and alcohol than the  $\alpha$ -anthrol. A solution of the compound, if heated in presence of air, is oxidised to a dark-green substance. The  $\beta$ -compound decomposes before it melts. With bromine it forms a bromine-product, and with sulphuric acid a sulpho-acid.

RECEIPTS FOR DYEING WITH NATURAL AND ARTIFICIAL ALIZARIN,  
PRINTING COLOURS WITH ARTIFICIAL ALIZARIN, CONTAINING 15  
PER CENT. OF DRY COLOURING-MATTER.

*For Red Grounds.*

800 grms. alizarin, at 15 per cent.  
1 kilo. acetic acid, at  $6^{\circ}$  B.  
2 litres water.  
200 grms. olive oil.  
200 „ acetate of lime, at  $10^{\circ}$  B.  
500 „ wheat-starch.

Boil well together, stir till cold, and add

200 grms. acetate of alumina, at  $15^{\circ}$  B.

*Very Dark Red.*

3300 grms. alizarin, at 15 per cent.  
10 litres thickening.  
490 grms. nitrate of alumina, at  $15^{\circ}$  B.  
600 „ acetate of alumina, at  $12^{\circ}$  B.  
500 „ acetate of lime, at  $16^{\circ}$  B.

*Red for Mille Fleurs Styles.*

2600 grms. alizarin, at 15 per cent.  
10 litres thickening for red (see A, p. 222).  
300 grms. nitrate of alumina, at  $15^{\circ}$  B.  
600 „ acetate of alumina, at  $12^{\circ}$  B.  
400 „ acetate of lime, at  $16^{\circ}$  B.

*Red without Oil.*

2800 grms. alizarin, at 15 per cent.  
 4800 „ acetic acid, at 8° B.  
 1800 „ flour.  
 2400 „ water.

Boil well, stir till cold, and add

487 grms. acetate of lime, at 16° B.  
 1000 grms. nitrate of alumina, at 15° B.  
 1500 „ hyposulphite of lime, at 9° B.

*Deep Red and Rose.*

1000 grms. alizarin, at 15 per cent.  
 8000 „ thickening.  
 500 „ acetate of alumina, at 12° B.  
 250 „ acetate of lime, at 16° B.

Rose is obtained by letting down 1 part of this colour with 2 to 3 parts of the thickening for reds.

In styles where a red ground is first printed on it, it must be steamed for an hour before printing the pattern, after which it is steamed for an hour, and aired for twenty-four hours. It is then passed through one or other of the following baths :—

1000 litres water.  
 60 lbs. chalk.  
 3 lbs. tin crystals, or :  
 1000 litres water.  
 40 lbs. chalk.  
 10 „ arseniate of soda.

The pieces are winced through at 122° to 144° Fahr., at such a speed that each remains in the bath from one to one and a-half minutes. They are then washed and cleared as follows :—

For 10 pieces of 50 metres—

1st soaping : 3 lbs. soap,  $\frac{1}{4}$  lb. tin crystals, at 122° F., half-an-hour.  
 2nd „ 3 lbs. soap, at 167° F., half-an-hour.  
 3rd „ 3 lbs. soap, at 167° to 178° F., half-an-hour.

Wash between each soaping.

*Thickening for Reds.*

## A.

6000 grms. wheat-starch.  
20 litres water.  
4 „ acetic acid, at 6° B.  
10 „ tragacanth mucilage (at  
2 ozs. gum tragacanth per litre).  
1500 grms. olive oil.  
Boil well together.

## B.

17 litres water.  
17 „ acetic acid, at 6° B.  
6 kilos. wheat-starch.  
1500 grms. olive oil.

*Nitrate of Alumina.*

1000 parts nitrate of lead, 1000 parts alum, 2000 parts (by weight) water. Nitrate of alumina gives the reds a yellower tone than does the acetate. When the former salt is used, more acetate of lime must be added.

*Acetate of Alumina (Red Liquor).*

15000 grms. hydrate of alumina (basic sulphate) are stirred into 6 litres acetic acid at 8° B., heated, filtered, and set at the strength required.

*Hydrate of Alumina.*

Dissolve 36 kilos. alum in 400 litres water, and precipitate, with a solution of 31 kilos. soda, in 400 litres of water. The precipitate is washed eight times by decantation, collected on a filter, and pressed. When a 15 per cent. alizarin paste is used, an addition of 30 per cent. of its weight of acetate of alumina, at 12° B., is generally requisite.

It is important to dissolve the hydrate of alumina in acetic acid always at one and the same temperature, 25° C., as the results cannot be otherwise constant.

*Acetate of Lime Solution.*

A solution at 16° B. contains 25 per cent. of acetate of lime. Well-washed alizarin-paste requires 15 per cent. of its weight of this solution. But for every fresh lot of alizarin the necessary quantity of acetate of lime should be experimentally determined.

*Printing Colour for Purples.*

900 grms. alizarin, at 15 per cent.  
10 litres thickening for violets.  
200 grms. acetate of iron, at 12° B.  
370 „ acetate of lime, at 16° B.

*Purple Thickening.*

5000 grms. starch.  
18 litres water.  
9 „ tragacanth mucilage (2 ozs. per litre of water).  
1000 grms. olive oil.

Boil well, and stir till cold.

The printed pieces are steamed for one to two hours at half an atmosphere, and then hung up for twenty-four to thirty-six hours. They are next passed, spread out in their full width, through the following mixture, in a cistern fitted with rollers, at the temperature of 122° to 144° F., for one and a half to two hours :—

1000 litres water.  
20 kilos. chalk.  
5 „ arseniate of soda.

They are next washed and soaped, at 144° to 167° F., for half-an-hour with 1500 grms. of soap per 10 pieces of 50 metres. After soaping, they are washed, dried, and finally slightly chlored, if needful.

An addition of arseniate of soda makes the violets much brighter.

Before introducing the pieces into the steam-chest, they must be carefully and perfectly dried. The best results are obtained with very dry pieces and very moist steam.

*Printing Colour for Browns.*

- 6000 grms. alizarin, at 15 per cent.
- 10 litres thickening.
- 900 grms. nitrate of alumina, at 18° B.
- 400 „ acetate of alumina, at 13° B.
- 400 „ red prussiate (previously dissolved in water).
- 500 „ acetate of lime, at 18° B.

To obtain a yellow shade, add 30 grms. bark liquor, at 20° B., per litre of colour.

To this brown colour any old spoiled red colours may be advantageously added, mixing with each 20 to 30 grms. of red prussiate of potash, dissolved in water, per litre.

*Dyeing with Purpurin.*

Purpurin dyes very readily, and without requiring the beck to be at a very high temperature.

*Dyeing Cottons.*

Goods mordanted for red, rose, and black, dye up very well, and a light soaping at 122° to 144° F. cleans the whites perfectly, and clears the colours sufficiently. The parts mordanted for purple dye up with the same ease, but the purples are greenish.

Purpurin is used for styles with white grounds, handkerchiefs, &c. It resists air and light well, but is not so permanent in boiling soap-becks. In such styles its use is very economical. One or 2 grms. give the fullest shades on a square metre or a handkerchief. A simple soaping renders the grounds perfectly white, and imparts the desired brilliance to the colours. Red and black handkerchiefs are preferably got up with purpurin, 2 grms. of which, with 5 grms. of sumach, dye a handkerchief perfectly the fullest red shade, whilst a single passage through bran after dyeing leaves the grounds perfectly white.

*Woollens (Yarn or Pieces).*

Wool dyes very well with purpurin. It is mordanted in the usual manner, with the addition of a little tannin for the red tones. The dyed goods require merely washing, and present then very brilliant shades, of a satisfactory permanence.

To prepare red steam colours with purpurin for goods mordanted with alumina, the following method is recommended:—Add to the purpurin 20 per cent. of its weight of soda, mix well, and add hot *soft* water. A splendid red colour is thus obtained, which is filtered, and allowed to cool a little. It is then mixed with starch-paste, so that the consistence may be fit for printing. The colour keeps for a long time without spoiling. After printing, the goods are steamed and washed. Twenty grms. of purpurin per litre yield a very full red. If, on filtering the solution of purpurin, any colouring-matter remains on the filter, it may be used in ordinary dyeing operations.

In dyeing wool with purpurin, we mordant as for garancin, either with tartar and alum or tartar and tin solution. The tin solution, which gives the best results, is—

|     |       |               |
|-----|-------|---------------|
| 300 | parts | nitric acid,  |
| 100 | „     | water,        |
| 50  | „     | sal-ammoniac, |
| 50  | „     | tin,          |

which is added gradually, the dissolving-pan being set in cold water. This solution is used after filtration.

To mordant the wool, it is entered in the beck at 30°, and raised in the course of an hour to 70° C. It is then taken out, wrung, and dyed in purpurin, entering at 30° C., and raising to a boil in half-an-hour.

The purpurin may be advantageously neutralised with a little soda or crystalline carbonate of ammonia. For this purpose it is put in a bottle, with a sufficient quantity of boiling water, and the alkaline carbonate is added. The whole is then poured into the dye-beck.

Wool mordanted with alum and tartar takes a very bright crimson. If mordanted with tartar and tin solution, it is dyed almost as fine a red as with cochineal, 2 to 4 grms. sufficing for a square metre of muslin or merino. To obtain a very bright orange-red, the wool is prepared with tartar and tin solution, to which a little young fustic or extract of fustic has been added. The whole is heated to 70° C. in a tin dye-pan, lifted, rinsed in flowing water, and dyed with purpurin as above. If the tone is not sufficiently orange, a little extract of young fustic may be added to the dye-beck.

Wool mordanted with alum is printed with purpurin in the same manner as cotton.

Purpurin can be fixed upon silk in the following manner:—The silk is mordanted with acetate of alumina, at 5° B., and dried or

prepared with precipitated alum, obtained by adding hydrate of alumina to common alum. Filter the solution when cold, and set it at 7° B. by the addition of water. The handkerchiefs are passed twice through this mordant, and dried at a steam heat. The next day they are passed through water at 50° C. In mordanting silk with acetate of alumina, a little chalk is added to the water. Dry at once, and stiffen with a little gum Senegal, or preferably tragacanth, at 2-5 grms. per litre.

The goods are then printed with the following colour :—32 grms. of purpurin, finely ground, are mixed with 1 litre of water, and 12 grms. soda-crystals are added. The purpurin dissolves perfectly in a few minutes, and the solution is strained through calico.

It is thickened with 200 grms. pale calcined starch, and the whole is then boiled. Print when the colour is cold, and steam with pressure when dry. Wash and soap in a weak clear soap-beck, at 40°-50° C., or even hotter. Half a gramme or a gramme of tannin may be added to the colour, dissolved in water holding 1 grm. of soda-crystals in solution.

Purpurin yields reds as deep as can be required, if the above-stated proportions between the colouring-matter and the soda are increased. All slightly alkaline salts may serve to dissolve purpurin. Borax or basic borate of soda is preferable, and dissolves rather more than soda-crystals; then follow the bicarbonates of soda and ammonia, carbonate of ammonia, potash, &c. Silicate of soda cannot be used, as under certain circumstances it yields gelatinous precipitates.

Purpurin, in dyeing mordanted silks, differs remarkably from madder or garancin. Its high tinctorial power admits of a very extended application, as the dye-becks can be perfectly exhausted.

Purpurin can also be employed in the form of aluminous lakes, red or rose. For this purpose either of the two following methods may be adopted :—

1. The solubility of purpurin in boiling salts of alumina is utilised; a solution of alum or other aluminous salt is heated, and purpurin is added, previously well ground up with water. The solution is allowed to cool down, and when luke-warm, a little chalk or soda is added, to hasten the precipitation of the lake.

2. The purpurin is dissolved in water containing a very little soda, and this solution is poured into that of an aluminous salt. The aluminous lake is formed immediately.

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